Tracing biogeochemical processes and anthropogenic impacts in granitic catchments: temporal and spatial patterns and implications for material turnover and solute export

Dissertation

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Summary

From a biogeochemical perspective, catchments can be regarded as reactors that transform the input of various substances via precipitation, deposition, or human activities as they pass through soils and aquifers towards receiving streams. Understanding and modeling the variability of solute concentration in catchment waters require the identification of prevailing processes, determining their respective contributions to the observed transformation of substances, their interplay with hydrological processes, and the determination of anthropogenic impacts. However, numerous biogeochemical processes often interact in a highly non-linear way and vary on temporal and spatial scales, resulting in temporally and spatially varying water chemistry in catchments. This is particularly true for riparian wetlands. Processes in this catchment area often superimpose the influence of the hill slope (and largest) area of the catchment on surface water quality.

Accordingly, the first part of this thesis (Study 1 and 2), focuses on the temporal and spatial variability of biogeochemical processes at the catchment scale. Therefore, the first aim was to identify the prevailing biogeochemical processes which affect the quality of catchment waters in two forested granitic catchments. Based on these results, (i) the long-term behavior of these processes was determined (Study 1) and (ii) hot spots of these processes at the catchment scale along different flow paths were identified (Study 2). The second part (Study 3) focuses on the interplay between hydrological and biogeochemical processes in a riparian wetland, with the aim of systematically tracing back the temporal patterns of stream water chemistry to different biogeochemical processes and antecedent hydrological boundary conditions in the wetland. The third part (Study 4 and 5) focuses on weathering processes with the goal (i) of identifying the mineralogical sources of the groundwater's buffer capacity against acid atmospheric deposition in a forested granitic catchment and (ii) determining the mineralogical sources of the high cation loads in surface water, induced by intensive agricultural activities in two agricultural granitic catchments. To reach these aims, multivariate statistical methods of dimensionality reduction (linear Principal Component Analysis, non-linear Isometric Feature Mapping), a low-pass filtering of time-series, a Cluster analysis, and major and trace element ratios and strontium isotopes were used.

A small number of biogeochemical process bundles explained 94% and 89% of the variance of the data set in Study 1 and 2, respectively. In Study 1, redox and topsoil processes, road salt and sulfate contamination were identified as predominating processes influencing water chemistry in the respective catchments. Low-pass filtered time series of component scores revealed a different long-term behavior at different sampling sites in both catchments, which could be traced back to the fraction of wetland area in the respective subcatchments as well as by the varying thickness of the regolith. Study 2 revealed that the upper 1 m topsoil layer could be considered as a biogeochemical hot spot for redox processes, acid-induced podsolization, and weathering processes along different flow paths. Up to 97% of the biogeochemical transformation of the chemical composition of soil solution,

groundwater and stream water in the Lehstenbach catchment was restricted to this soil layer representing less than 2% of the catchment's regolith.

Wetland stream water, mobilized in the topsoil layer being considered a biogeochemical hot spot, showed a highly dynamic temporal pattern of component scores. Study 3 revealed four different types of wetland stream water chemical status, depending on the interplay between discharge dynamics, biological activity, and the water table position in the wetland. The sequence of different stream water types roughly followed a seasonal pattern, albeit being heavily modified by the respective hydrological boundary conditions for different years. Extended periods of low groundwater level in the second half of the growing season drastically changed the chemical boundary conditions, becoming evident in a drastic reoxidation of reduced species like sulfides and corresponding effects.

Weathering processes are one of the predominating biogeochemical process bundles influencing water chemistry in forested catchments. Study 4 showed that the mineralogical sources of the groundwater's buffer capacity against acid atmospheric deposition were dominated by the release of base cations from apatite dissolution, preferential cation release from feldspars and biotite, and feldspars weathering.

In Study 5, determining the mineralogical sources of the high cation loads in surface water induced by intensive agricultural activities revealed a dominant manure contribution in the topsoil, and enhanced mineral dissolution (plagioclase and biotite) by fertilizer application in subsoils, becoming the unique source of base cations in the saprolite. Stream water chemistry differed from that of soil water, suggesting that stream water chemistry was dominated by elements issued from enhanced mineral and rock weathering. Soil acidification induced by agriculture allows the mobilization of cations stored in soil layers, enhances the rock weathering and accelerates plagioclase dissolution, which can highly influence stream water quality.

Numerous biogeochemical, hydrological, and anthropogenic processes were found to interact with each other, mostly with non-linear patterns, influencing catchment water chemistry. The integral approach used in this thesis would be a useful prerequisite to develop accurate and parsimonious models commonly used for water management purposes by distinguishing between short- term and long-term shifts, reducing the number of processes to the predominating ones ultimately to be included in the model, focusing on hot spots and including spatial patterns where necessary and appropriate.

Zusammenfassung

Aus einer biogeochemischen Perspektive können Einzugsgebiete als Reaktoren betrachtet werden, die Substanzen, welche durch Niederschläge, Deposition oder menschliche Aktivitäten eingetragen werden, auf ihrem Weg durch Böden und das Grundwasser zum Vorfluter transformieren. Um die Variabilität von Stoffkonzentrationen in den Wässern von Einzugsgebieten zu verstehen und zu modellieren, ist es nötig, die vorherrschenden Prozesse, ihren jeweiligen Beitrag zum Stoffumsatz, ihr Zusammenspiel mit hydrologischen Prozessen sowie menschliche Einflüsse auf den Wasserchemismus zu bestimmen. Allerdings interagieren zahlreiche biogeochemische Prozesse oft hochgradig nicht-linear miteinander und variieren auf verschiedenen zeitlichen und räumlichen Skalen, was dazu führt, dass sich der Chemismus der Wässer im Einzugsgebiet zeitlich und räumlich ändert. Dies gilt insbesondere für ufernahe Feuchtgebiete. Prozesse in diesem Teil des Einzugsgebiets überlagern oft den Einfluss des Oberhangs, d.h. des größten Teils des Einzugsgebiets, auf die Qualität von Oberflächenwasser.

Dementsprechend wurde im ersten Teil dieser Dissertation (Studie 1 und 2) auf die zeitliche und räumliche Variabilität von biogeochemischen Prozessen auf Einzugsgebietsskala abgezielt. Ziel war es, zunächst die vorherrschenden biogeochemischen Prozesse zu identifizieren, welche die Wasserqualität in zwei bewaldeten Granit-Einzugsgebieten beeinflussen. Basierend auf diesen Ergebnissen wurde (i) das Langzeitverhalten dieser Prozesse untersucht (Studie 1) und wurden (ii) „hot spots“ dieser Prozesse entlang von verschiedenen Fließwegen bestimmt (Studie 2). Im zweiten Teil (Studie 3) wurde das Zusammenspiel zwischen hydrologischen und biogeochemischen Prozessen in einem ufernahen Feuchtgebiet untersucht mit dem Ziel, zeitliche Muster im Bachwasserchemismus systematisch verschiedenen biogeochemischen Prozessen und hydrologischen Randbedingungen im Feuchtgebiet zuzuordnen. Im dritten Teil (Studie 4 und 5) wurden Verwitterungsprozesse untersucht mit dem Ziel, (i) die mineralogische Herkunft der Pufferkapazität des Grundwassers gegen saure atmosphärische Deposition in einem bewaldeten Granit-Einzugsgebiet zu bestimmen und (ii) die mineralogische Herkunft der hohen durch intensive Landwirtschaft hervorgerufenen Kationenladung im Bachwasser in zwei landwirtschaftlich genutzten Granit-Einzugsgebieten zu ermitteln. Um diese Ziele zu erreichen, wurden multivariate statistische Methoden der Dimensionsreduzierung (lineare Hauptkomponentenanalyse, nicht-lineares Isometric Feature Mapping), Tiefpass-gefilterte Zeitreihen, eine Cluster-Analyse sowie Haupt- und Spurenelementverhältnisse und Strontiumisotope angewendet.

Eine kleine Anzahl biogeochemischer Prozesse erklärten 94% bzw. 89% der Varianz des Datensatzes in Studie 1 bzw. Studie 2. In Studie 1 konnten Redox- und Oberbodenprozesse, Straßensalz- und Sulfatkontamination als vorherrschende Prozesse identifiziert werden, welche die Wasserqualität in den Einzugsgebieten beeinflussen. Tiefpass-gefilterte Zeitreihen der Komponentenwerte verschiedener Probenahmestellen der zwei Einzugsgebiete zeigten nicht-lineare Trends. Es konnte gezeigt werden, dass dieses unterschiedliche Langzeitverhalten vom Flächenanteil an Feuchtgebieten bzw. einer unterschiedlichen Mächtigkeit der Verwitterungsschicht abhängt. Studie 2 zeigte, dass die oberste 1 m

mächtige Bodenschicht als biogeochemischer „hot spot“ für Redox-Prozesse, säure-induzierte Podsolierung und Verwitterungsprozesse entlang von Oberhang- und Feuchtgebietsfließwegen betrachtet werden kann. Bis zu 97% der biogeochemischen Umwandlungsprozesse, welche die chemische Zusammensetzung von Bodenlösung, Grund- und Bachwasser im Einzugsgebiet Lehstenbach beeinflussen, spielten sich in dieser Oberbodenschicht ab, die weniger als 2% des Gesamtvolumens des Einzugsgebiets ausmacht.

Bachwasser aus dem Feuchtgebiet, das in der Oberbodenschicht mobilisiert wird, die als biogeochemischer „hot spot“ betrachtet werden kann, zeigte ein dynamisches zeitliches Muster der Komponentenwerte. In Studie 3 konnten vier Typen des Bachwasserchemismus in Abhängigkeit des Zusammenspiels von Abflussdynamik, biologischer Aktivität und dem Grundwasserniveau im Feuchtgebiet unterschieden werden. Die Abfolge der verschiedenen Typen folgte größtenteils einem saisonalen Muster, wurde allerdings deutlich durch von Jahr zu Jahr wechselnde hydrologische Randbedingungen modifiziert. Längere Zeiten mit niedrigem Grundwasserniveau in der zweiten Hälfte der Vegetationsperiode veränderten stark die chemischen Randbedingungen, was sich in einer drastischen Aufoxidierung von reduzierten Verbindungen wie Sulfiden und ähnlichen Effekten zeigte.

Verwitterungsprozesse gehören zu den vorherrschenden Prozessen, welche die Wasserqualität in bewaldeten Einzugsgebieten beeinflussen. Studie 4 zeigte, dass die Pufferkapazität des Grundwassers gegen saure atmosphärische Deposition v.a. auf Apatitlösung, präferentielle Freisetzung von Kationen aus Feldspäten und Biotit sowie auf die Verwitterung von Feldspäten zurückzuführen ist.

Die Bestimmung der mineralogischen Herkunft der durch intensive Landwirtschaft hervorgerufenen hohen Kationenladung im Bachwasser in Studie 5 ergab einen vorherrschenden Einfluss durch Gülle und Mist im Oberboden sowie durch Düngemitteleinsatz verstärkte Mineral-Lösungsprozesse (Plagioklas und Biotit) im Unterboden, welche die einzige Kationenquelle in der Verwitterungsschicht darstellten. Bachwasser hatte im Vergleich zur Bodenlösung eine unterschiedliche chemische Zusammensetzung, was auf einen entscheidenden Einfluss von Verwitterungsprozessen auf den Bachwasserchemismus schließen ließ. Die durch die Landwirtschaft hervorgerufene Bodenversauerung führt zu einer Mobilisierung von Kationen aus dem Boden, verstärkten Mineral-Lösungsprozessen sowie einer beschleunigten Plagioklas-Verwitterung.

Zahlreiche biogeochemische, hydrologische und anthropogene Prozesse interagieren meist auf nicht-lineare Weise miteinander, was einen entscheidenden Einfluss auf den Wasserchemismus in Wassereinzugsgebieten hat. Der in dieser Dissertation angewandte umfassende Ansatz schafft eine Grundvoraussetzung zur Entwicklung von zielführenden und schlanken Modellen, die üblicherweise für Wassermanagementaufgaben verwendet werden, und zwar durch die Unterscheidung zwischen Kurzzeit- und Langzeitveränderungen, durch die Reduzierung der Anzahl der ins Modell implizierten Prozesse auf die vorherrschenden Prozesse, durch Fokussierung auf „hot spots“ und durch Berücksichtigung von räumlichen Mustern, wo es nötig und angebracht erscheint.

1. Introduction

Catchments can be regarded as reactors for various dissolved inorganic and organic substances (Fig. 1). Gaseous, dissolved and particulate substances from outside a catchment (elemental input) together with substances originating from the catchment itself are cycled within the catchment by a multitude of biogeochemical processes in the soil and in the groundwater. Thereby, substances are transported by infiltrating rain water, fog and snow melt water through the catchment or by surface runoff on the soil surface towards receiving streams (Neal et al., 1997a; Stutter et al., 2006). Thus, a fraction of the substances will leave the catchment (elemental export), either in dissolved form or as gaseous or particulate compounds. In general, the quality of catchment waters is affected by various biogeochemical, hydrological, and anthropogenic processes that take place along different flow paths within the catchment.

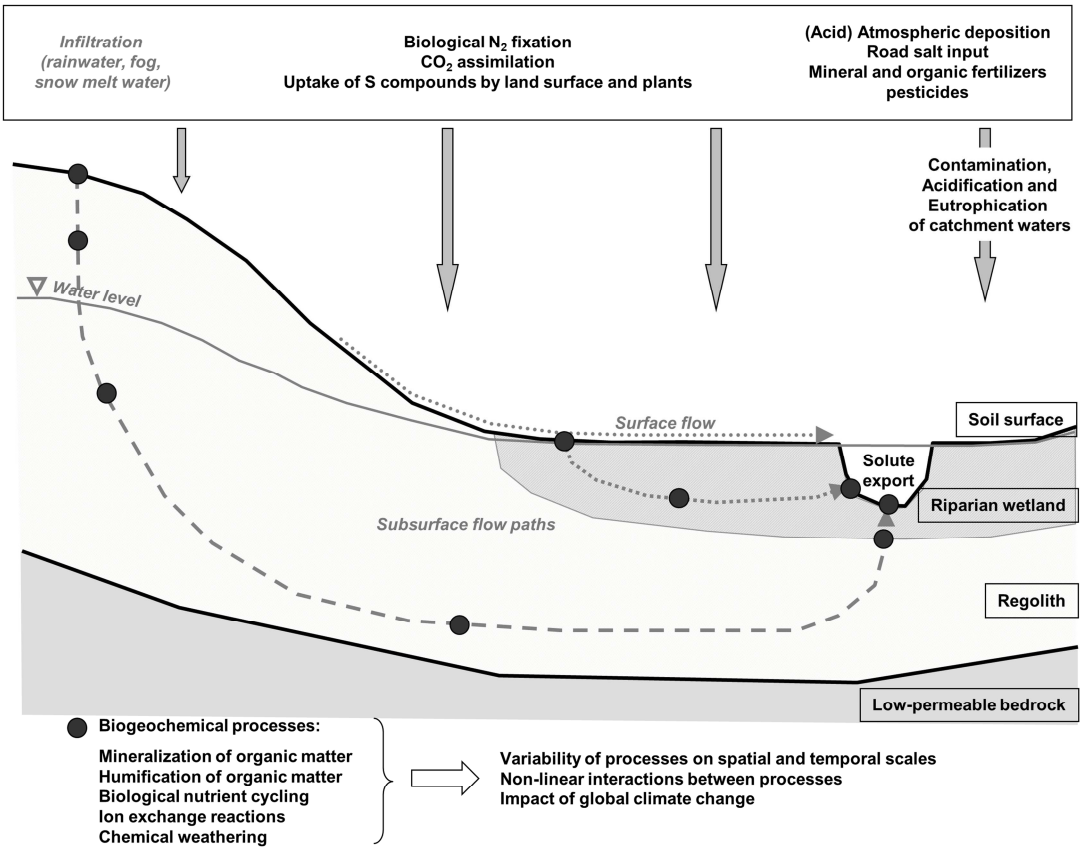

Fig. 1: Overview of hydrologic, biogeochemical and anthropogenic processes and solute sources influencing water quality in forested and agricultural (granitic) catchments. Biogeochemical processes exhibit variability on different spatial and temporal scales. The different processes interact in a non-linear way and are influenced by global climate change.

1.1 Elemental input to the ecosystem

Natural and anthropogenic sources contribute to the ecosystem elemental input to varying extent from catchment to catchment. Natural processes like biological nitrogen fixation, carbon assimilation or

uptake of sulfur compounds by land surface and plants are important for primary production and nutrient balance as well as for N, C and S budgets in ecosystems. Besides, human activities, in addition to natural processes, lead to considerable inputs of substances in catchments and thus can alter the quality of soil-, ground- and stream waters (Fig. 1). For example, in natural catchments, acid atmospheric deposition (H^+, S-compounds) originating from industrial activities has been an important and increasingly significant cause of soil, surface water and groundwater acidification in Europe since the Industrial Revolution (e.g. Futter et al., 2014; Garmo et al., 2014). Acid atmospheric deposition is still of major concern in catchments with acid-sensitive soils, like forested silicate ecosystems, despite a significant reduction in the last 20 years (Likens et al., 1998; Stoddard et al., 1999; Armbruster et al., 2003; Borg and Sundbom, 2014). The application of road salt has adverse effects on water quality (Godwin et al., 2003; Rhodes and Guswa, 2016), leads to higher nutrient leaching, and can suppress the recovery of natural ecosystems from acidification (Schweiger et al., 2015). In agricultural catchments, the application of pesticides and mineral and organic fertilizers on soil cause contamination and eutrophication of catchment waters (e.g. Kurilic et al., 2015; Nguyen et al., 2015a; Fig. 1). The application of high amounts of ammonium-based fertilizers in intensive agriculture is known to cause significant soil acidification down to subsoil layers (Ganev, 1992; Graham et al., 2002; Guo et al., 2010; Meng et al., 2014), which would require vast amounts of lime to neutralize (Guo et al., 2010). Soil acidification has dramatic consequences on metal mobilization and plant uptake (Goulding and Blake, 1998) as well as on base cation export (Huang et al., 2015).

1.2 Processes within the catchment

In the subsurface, water does not become completely mixed, but follows distinct flow paths (Hill, 1990; Church, 1997; Rademacher et al., 2005; Biggs et al., 2006). Along these flow paths, a variety of biogeochemical processes occur (Fig. 1) that modify the concentration of various dissolved organic and inorganic substances (Soulsby et al., 1998; McClain et al., 2003; Biggs et al., 2006; Yang et al., 2012), including mineralization (e.g. Stemmer et al., 2000; Morse et al., 2014) and humification of organic matter (e.g. Zech et al., 1992; Schwesig et al., 2003; Schnitzer and Monreal, 2011), biological nutrient cycling (e.g. Morse et al., 2014; Edokpa et al., 2015), ion exchange reactions (e.g. Redwan et al., 2016; Sethy et al., 2016) and chemical weathering processes (e.g. Redwan et al., 2016; Sethy et al., 2016). Along the flow paths, the different biogeochemical processes vary on spatial and temporal scales, and exhibit varying reaction rates. Short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods are defined as biogeochemical hot moments, and patches that show disproportionately high reaction rates relative to the surrounding matrix are defined as biogeochemical hot spots (McClain et al., 2003). Such hot moments and hot spots that exist at different temporal and spatial scales (McClain et al., 2003) can be responsible for a large part of the material turnover in ecosystems (Vidon et al., 2010; Morse et al., 2014). For example, Groffman et al. (2009a) pointed out that hot spots play an important role in the denitrification activity in ecosystems,

which in turn increases the uncertainty of denitrification models (Groffman et al., 2009b; Pinay et al., 2015). Thus, systematically identifying and characterizing these hot moments and hot spots would be critical to understanding and modeling biogeochemical processes in catchments (McClain et al., 2003; Groffman et al., 2009a; Vidon et al., 2010; Morse et al. 2014; Bernhardt et al., 2017).

Besides spatial and temporal variations of catchment processes, numerous interactions exist between biogeochemical, anthropogenic and hydrological processes in the catchment. Such interactions were investigated and modeled in numerous studies: the interplay of different biogeochemical processes and their interaction with hydrological processes e.g. by Church (1997), McClain et al. (2003), Stutter et al. (2006) and Gao et al. (2014), their relation to the catchment's structure and properties e.g. by Church (1997), Biggs et al. (2006), Stutter et al. (2006) and Grathwohl et al. (2013) as well as anthropogenic impacts on catchment processes (e.g. Négrel et al. 2007; Marghade et al., 2015; Shin et al., 2014), including acid atmospheric deposition (e.g. Hruška et al., 2002; Huang et al., 2013), agriculture (Dupas et al., 2017) and global climate change (e.g. Mitchell, et al., 2006; Szkokan-Emilson et al., 2013; Clargo et al., 2015). Interactions between biogeochemical, anthropogenic and hydrological processes can largely influence catchment water chemistry and can be relevant on all scales, from the micro-scale (Reina et al. 2015), the catchment scale (Cirmo and McDonnell, 1997; Fleckenstein et al., 2011; Gao et al., 2014; Gottselig et al., 2017) up to the global scale (Guo et al., 2015; Rüegg et al. 2015; Leach et al 2016). Many of these processes turned out to interact in both a non-linear way and via feedback loops. Thus, the determination of the dominant biogeochemical, anthropogenic, and hydrological processes at large scales is often complicated, but is crucial to water resources management.

The temporal and spatial variability of catchment processes and their manifold interactions result in a catchment water chemistry that varies widely across temporal and spatial scales, from short-term to long-term (e.g. Mast, 2013; Daneshvar, 2015; Nguyen et al., 2015b; Lloyd et al., 2016) and from molecular to global (e.g. Knorr et al., 2007; Schot and Pieber, 2012; Ulanowski and Branfireun, 2013; Soumya et al., 2013; Clargo et al., 2015). Spatial and temporal variations of solute concentration were found in all water sources in catchments, in soil solution (e.g. Schön et al., 2016), groundwater of upslope zones (e.g. Kaba et al. 2016), wetland groundwater (Schot and Pieber, 2012; Ulanowski and Branfireun, 2013), and surface waters (Neal et al., 1997a; Zimmer et al. 2013). Inferring which processes have an impact on the quality of catchment waters – and to what degree – by assessing spatial and temporal patterns of solutes or species, and to relate them to hydrological and biogeochemical processes (e.g. Christophersen et al., 1982; Fröhlich et al., 2008; Kerr et al., 2008; Lloyd et al., 2016) is the challenge of environmental monitoring. Many studies used single indicator parameters that were assumed to be very closely related to single processes. However, this approach is limited to certain boundary conditions. In more recent times, there has been an increasing number of studies that have focused on a multitude of solutes and processes (Zhang et al., 2014; Maassen et al., 2015; Moya et al., 2015; Yang et al., 2015). Elucidating the complex interplay between different

processes within the catchment, and distinguishing between different effects are requirements to developing strategies in water resources management. Small-scale effects have to be distinguished from more general patterns that are typical for large regions, and natural sources of spatial and temporal variability including heterogeneity of soil properties and interannual climatic variability have to be differentiated from anthropogenic impacts or effects of long-term climate change (e.g. Aubert et al., 2013b; Boettcher et al., 2014; Shin et al., 2014). The spatial and temporal scale used to study these effects has to be adapted to that of the process or effect of interest. In fact, effects of long-term climate change are not detectable on the base of short-term investigations of a few months or a few years. In contrast, it requires decades to observe their dynamics and to evaluate their consequences (Müller et al., 2010; Lutz et al., 2012; Mast, 2013; Borg and Sundbom, 2014). In addition, long-term shifts do not necessarily show up as linear trends, and in fact rarely do so for longer periods.

Chemical weathering, which is considered to be one of the dominant processes impacting stream water, groundwater and soil water quality (Lin et al., 2012; Bestland and Stainer, 2013; Sheikh et al., 2014; Thomas et al., 2014), can be seen as an example for the spatial and temporal variability of catchment processes on different scales and its interaction with hydrological and anthropogenic processes. The intensity of chemical weathering varies along different flow paths, and is in general more intense in deeper soil layers (Shand et al., 2007; Buss et al., 2017). Likewise, weathering processes vary spatially also at the small scale, i.e. from mineral grain to mineral grain. In fact, the role of accessory minerals like apatite or calcite in granite catchments in base cation release (Clow et al., 1997; White et al., 1999; Blum et al., 2002; Oliva et al., 2004) is controversially discussed in the literature, although the most abundant minerals, i.e. plagioclase, potassic feldspar, biotite and muscovite (Lasaga et al., 1994; Sverdrup and Warfvinge, 1995; Goulding and Annis, 1998; Probst et al., 2000), are considered to be the main source of base cation supply in silicate bedrock. At the temporal scale, long-term weathering rates can differ from the contemporary ones (Buss et al., 2017). Anthropogenic acidifying inputs, like acid deposition (Calmels et al., 2011; Huang et al., 2013; Kaushal et al., 2013; Guo et al., 2015) or physiological acid fertilizers (Fortner et al., 2012; Meng et al., 2014), are known to enhance weathering processes in soils and in deep groundwater. In addition, weathering processes are influenced by and exert control on global climate change due to their interaction with CO_2 concentrations in the atmosphere (Beaulieu et al., 2012; Li and Ji, 2015; Wan et al., 2017).

1.3 Solute export

Regarding catchments as biogeochemical reactors, a fraction of various chemical substances originating from natural and anthropogenic sources that have been transformed within the catchment by numerous biogeochemical and hydrological processes interacting in a highly (non-linear) way along different flow paths will leave the system as elemental export in the form of gaseous compounds, (Goldberg et al., 2008; Knorr et al., 2008; Gomez et al., 2016), solute export with stream water (Yusop

et al., 2006; Gao et al., 2014; Fasching et al., 2016) or in particulate form (Yusop et al., 2006; Dhillon and Inamdar, 2014; Gao et al., 2014; Fig. 1). With respect to solute export, numerous studies in different disciplines of Earth Sciences investigated dynamics in stream water solute concentration in order to determine solute sources, to elucidate temporal and spatial variations, and to deduce the controlling hydrological, biogeochemical or anthropogenic processes (e.g. Hamilton et al. 1997; Oswald and Branfireun, 2014; Fasching et al. 2016; Musolff et al., 2017). Hydrologists aim at understanding hydrochemical variations in stream water by investigating hydrological flow paths. Solute concentrations in stream water are related to solute concentrations in soil- and groundwater in order to ascribe systematic shifts in stream water solute concentration during stormflow periods to changes in water flow paths (Christophersen et al., 1982; Davies et al., 1992; Hagedorn et al., 2000; Lyon et al., 2011), which in turn would result in different types of runoff events (Emmett et al,. 1994; Bechtold et al., 2003; Inamdar et al., 2008; Bauwe et al., 2015). However, this approach implies that the chemical composition within a single water component does not change with respect to time and space, which presumably holds only at the time scale of single stormflow periods. In contrast to hydrologists, biogeochemists generally focus on internal biogeochemical processes, elemental and nutrient sources, and cycling in soils and catchments (Koba et al. 1997; Legout et al. 2005; Morse et al. 2014; Mettrop et al. 2014,). However, biogeochemists generally do not relate biogeochemical processes within the catchment to changes in stream water chemistry. Environmental scientists, however, focus on the interplay between biogeochemical and hydrological processes in catchments and on the implications for solute export in streams (Emili and Price, 2013; Gao et al., 2014; Sebestyen et al., 2014; Lloyd et al., 2016).

Processes in the riparian wetlands often superimpose the influence of the hill slope (and largest) area of the catchment (Hooper, 2001; Prior and Johnes, 2002; Piatek et al., 2009; O'Brien et al., 2013). Thus, understanding the interplay between hydrological and biogeochemical processes affecting solute export from that part of the catchment is of great interest and was the objective in various studies, investigating fluctuating climatic conditions (Kull et al., 2008), seasonal factors (Muller and Tankéré-Muller, 2012; Broder et al., 2017) like seasonal hydrologic events (Kerr et al., 2008), changes in the water flow pathways (Christophersen et al., 1982; Mitchell et al., 2006; Kerr et al., 2008), antecedent moisture conditions (Mitchell et al., 2006; Inamdar et al., 2009; Broder et al., 2017), redox processes (Kerr et al., 2008), available solute concentration in the wetland (Piatek et al., 2009), dilution of solutes (Inamdar et al., 2009), the flushing of solutes after drought periods (Emmett et al., 1994; Szkokan-Emilson et al., 2013), and both hydrological and redox preconditions in the wetlands (Knorr, 2012; catchment of this study). However, the interplay between the different processes and the implications for solute export from wetland sites is not yet fully understood: further research is required. In particular, hydrological extreme events like long dry periods and heavy rainstorms are predicted to increase in frequency and intensity due to climate change. Consequently, a change of biogeochemical processes in the riparian wetlands is likely, and will thus directly influence surface

water quality (Emmett et al., 1994; Kull et al., 2008; Ledesma et al., 2013; Szkokan-Emilson et al., 2013).

Overall, knowing the dominant hydrological, biogeochemical, and anthropogenic processes and their interactions that affect water quality in catchment waters is crucial for strategies in water resources management (e.g. Wang et al., 2015; Zheng et al., 2015; Lloyd et al., 2016). However, despite numerous studies in that field aimed at understanding the soil-groundwater-stream hydrochemical system, no comprehensive process model yet explaines in detail the overall catchment hydrochemical interactions (Kirchner, 2003). Thus, there is still a need to better understand processes causing chemical signatures in runoff (Kirchner, 2003; Aubert et al., 2013a; Dhillon and Inamdar, 2014). An integral approach is needed to fully understand the function and the processes in catchments and to predict their responses to environmental change (Wang et al. 2015).

2. Research objectives

The overall goal of this thesis was to achieve a better understanding of the complex interplay between geochemical, biological, hydrological and anthropogenic processes and factors of influence on water quality in situ, i.e., at the catchment scale. The studies were restricted to Variscan granite regions in order to keep bedrock lithology comparable, and because the weathering rate of granite (Meybeck, 1987) and the resulting buffer capacity against acidifying deposition or agricultural nutrient load is fairly low.

Addressing the comprehensive objective required a combination (i) of various types of data, i.e. solute concentration and Sr isotopes in soil solution, groundwater, and stream water as well as solid phase elements in rock minerals and soils, and (ii) of various methods using field data, i.e. element concentration ratios and Keeling diagrams, multivariate statistical methods of dimensionality reduction (linear Principal Component Analysis (PCA), Isometric Feature Mapping (Isomap; Tenenbaum et al., 2000) and Cluster analysis), and a low-pass filtering of long-term time series.

All the studies were based on the following basic assumptions:

(i) A transport and biogeochemical continuum of well-drained soils, wetland soils, deep groundwater and stream water exists in the respective granitic catchments.

(ii) A small number of prevailing processes occur everywhere in the catchments and at any point in time, but to varying degrees.

In the first part of this thesis, the goal was to elucidate the complex interplay between different biogeochemical processes that influence water quality by identifying the prevailing ones (Study 1 and 2) and by investigating their temporal and spatial variability at the catchment scale. Thus, the focus was to

(i) determine the long-term behavior of the prevailing processes (Study 1), and to

(ii) identify hot spots of the prevailing processes at the catchment scale along different flow paths (Study 2).

In the second part, the focus was on the interplay between hydrological and biogeochemical processes in a riparian wetland identified as a hot spot of biogeochemical catchment processes in Study 2 close to the discharging stream. The aim was to systematically trace back the temporal patterns of stream water chemistry to different biogeochemical boundary conditions in the wetland, which were in turn related to the antecedent hydrological boundary conditions in the wetland (Study 3).

Long-term trends of biogeochemical processes have turned out to be related to the varying thickness of the regolith in Study 1, which is directly related to weathering processes. In addition, the release of base cations, Si, and Al via weathering have been determined as one of the dominant biogeochemical processes in Study 1 and 2. Thus in the third part, the focus was on weathering processes influenced by anthropogenic inputs with the goal of

(i) ascertaining the mineralogical sources of the groundwater's buffer capacity against acid atmospheric deposition in a forested catchment (Study 4), and of

(ii) determining the mineralogical sources of the high cation loads in surface waters, induced by intensive agricultural activities in two small and adjacent granitic catchments where intensive agriculture predominates (Study 5).

3. Study Sites

3.1 Lehstenbach catchment, Bavaria, Germany

The Lehstenbach catchment (50°08'N and 11°52'E) is located in the Fichtelgebirge Mountains, near the German-Czech border in SE Germany (Gerstberger et al., 2004; Fig. 2 and Fig. 3). The watershed area is 4.19 km^2 and elevation ranges from 690 m to 877 m a.s.l.. Bedrock is variscan granite of two different facies (Besang et al., 1976), which show very similar mineralogical composition composed of quartz (36%), K-feldspar (29–38%), plagioclase (17–24%), biotite and muscovite (8–10%) and accessory minerals like apatite (<0.5%).

The thickness of the regolith is up to 40 m and more due to intensive tertiary weathering (Lischeid et al., 2002). Dystric cambisols and podzols predominate. Fibric histosols and dystric gleysols are found in the riparian zone, representing about one third of the watershed area (Küsel and Alewell, 2004). Soils are strongly acidified showing a pH(H_2O) in the A-horizon as low as 3.70 (Gerstberger et al., 2004). The climate is humid-continental, annual mean air temperature is 5.75°C and annual mean precipitation is between 950 and 1250 mm. Dense Norway spruce stands cover more than 95% of the

watershed area. Snow pack usually develops in January and final snowmelt occurs in March (Lischeid et al., 2002).

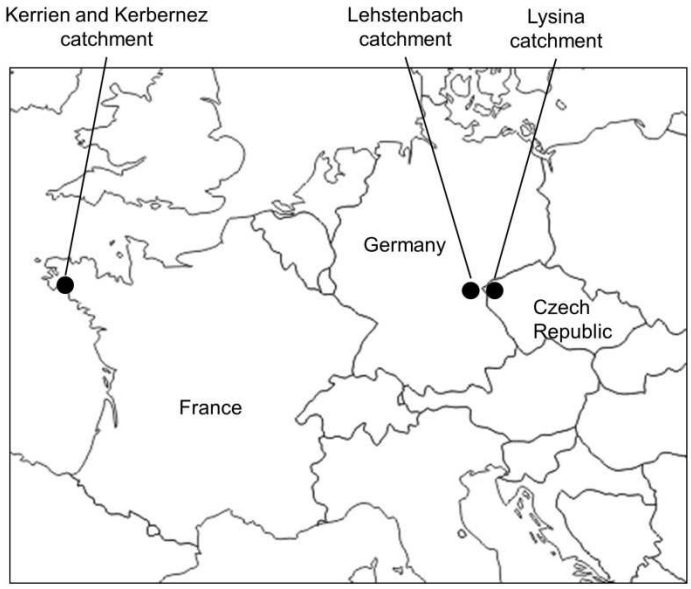

Fig. 2: Location of the Kerrien and Kerbernez catchments in France, the Lehstenbach catchment in Germany, and the Lysina catchment in the Czech Republic, respectively.

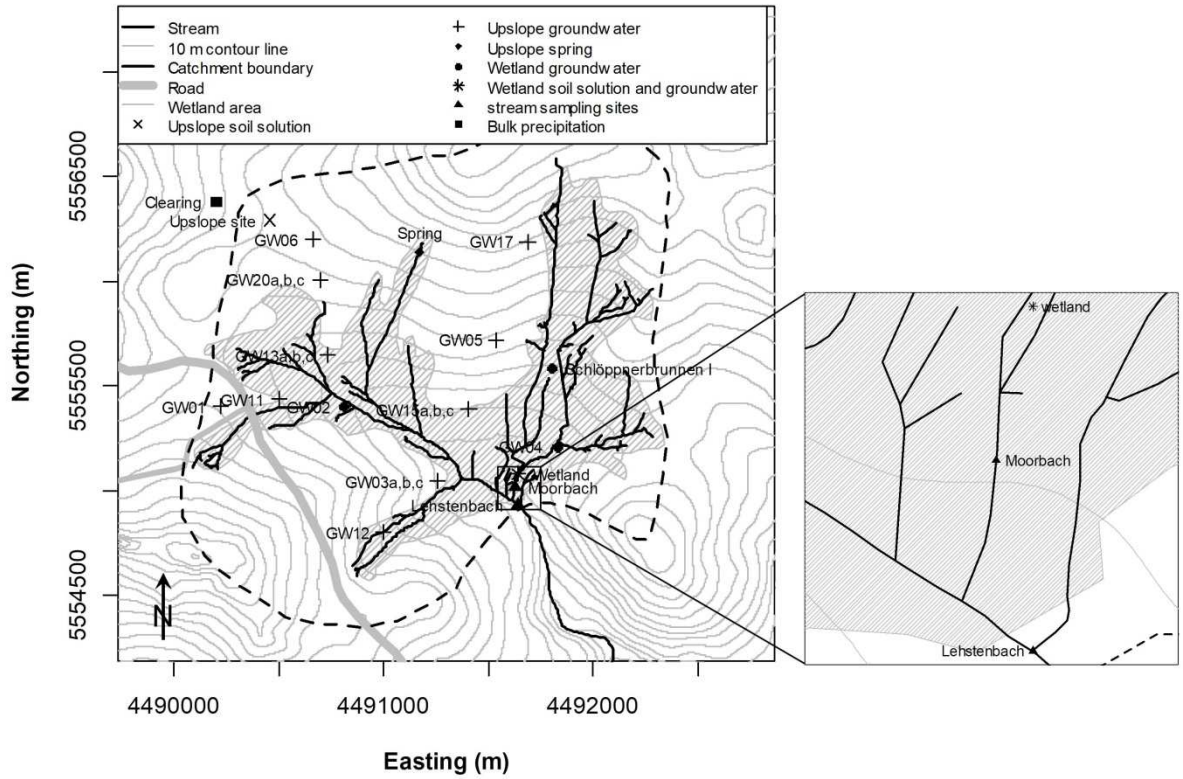

Fig. 3: Map of the Lehstenbach catchment in the Fichtelgebirge Mountains in southeast Germany and sampling sites.

Groundwater circulates mainly in the regolith that can be considered as a porous aquifer with a saturated hydraulic conductivity of about $3 \cdot 10^{-6}$ m s^{-1}. Mean residence time of water measured at the catchment outlet is 3.6 years (Lischeid et al., 2002). Mean groundwater level is close to the surface

during the whole year in the riparian zone, and more than 10 m below the surface in the upper part of the catchment.

The area is drained by a dense network of natural streams and artificial channels. Annual mean runoff was 470 mm in the 1991 to 2001 period (Lischeid et al., 2010). Groundwater flow in the regolith parallel to the stream at the catchment outlet is likely to be a negligible portion of the total outflow (Lischeid et al., 2002). Stream discharge is generated by deep groundwater recharge during base flow conditions even during longer dry periods. During heavy rainstorms the riparian zone is hydrologically connected to the stream leading to a strong increase in stream discharge during heavy rainstorms (Lischeid et al., 2002). The slightly acidic Schlöppnerbrunnen fen near the catchment outlet is drained by the ephemeral Moorbach stream. The fen area is 0.08 km^2 and peat accumulation ranges between 30 and 70 cm.

The watershed is still highly affected by atmospheric deposition (sulphur oxides, nitrogen oxides, protons, base cations) that peaked in the 1970s and steadily decreased thereafter (Matzner et al., 2004). The catchment has been limed with dolomite several times in the past, excluding the riparian zone and selected study plots. In general, Ca and Na are the predominant cations in streams and groundwater (Lischeid et al., 2004). The waters are acid and mostly hydrogen-carbonate free with a pH between 3.3 and 6.

3.2 Lysina catchment, western Czech Republic

The Lysina catchment is situated in the mountain region of the Slavkov Forest in the western part of the Czech Republic (50°03'N and 12°40'E; Fig. 2 and Fig. 4). The catchment area is 0.273 km^2, the elevation ranges between 829 and 949 m a.s.l. and the thickness of the regolith is about 2.5 m. Annual mean precipitation of the 1991–2001 period was 933 mm, annual mean air temperature was about 5.2°C, and annual mean runoff was 432 mm. Snowpack usually develops in December or January and final snowmelt occurs in March or April.

The Lysina catchment is located at about 60 km distance from the Lehstenbach catchment and exhibits the same geology, soil types, land use and atmospheric deposition history. However, in contrast to the Lehstenbach catchment, at Lysina, nitrogen deposition between 1998–2000 was only 73% of that between 1991–1993 (Hruška et al., 2002), and the nitrate peaks in the winter season started to decrease at the end of the 1990s. A detailed description of the site is given in Hruška et al. (2002).

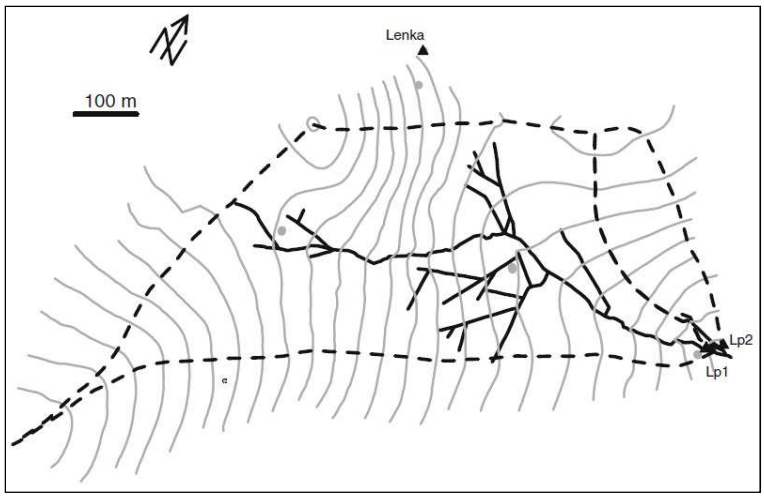

Fig. 4: Map of the Lysina catchment in the western Czech Republic (Lischeid et al., 2010).

3.3 Kerbernez and Kerrien catchments, Brittany, France

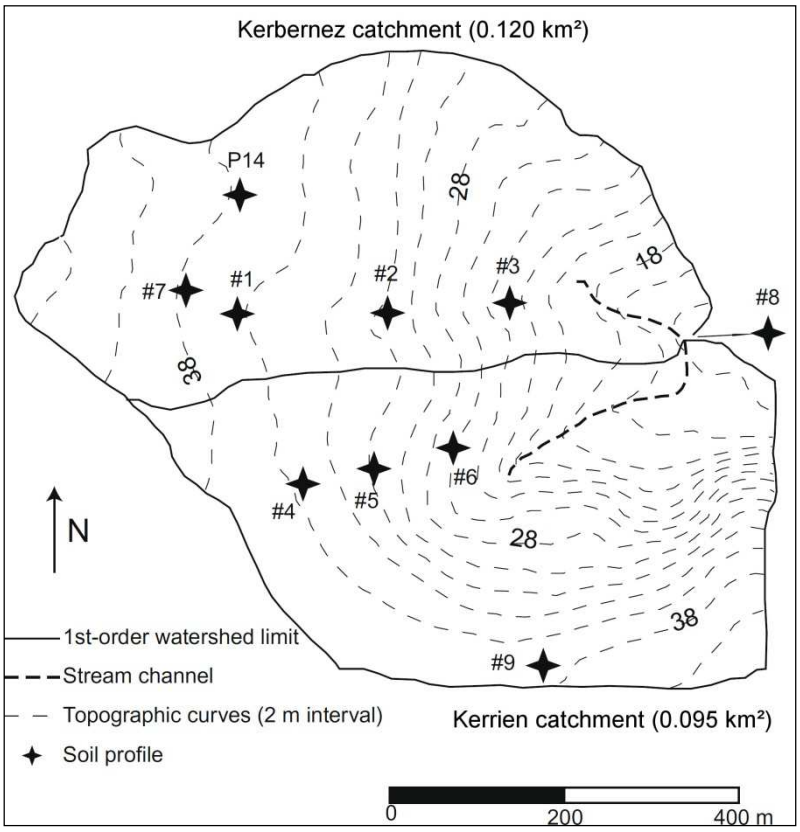

Fig. 5: Map of the Kerbernez and Kerrien catchments in Brittany, northwestern France, with the different sampling sites (soils and streams) (Pierson-Wickmann et al., 2009).

The Kerbernez and Kerrien catchments are located in south-western Brittany, France (47°57'N and 4°8'W), roughly 550 km west of Paris (Fig. 2 and Fig. 5). In this region, intensive agriculture has been developed since the late 1960s. Kerrien (0.095 km^2) and Kerbernez (0.120 km^2) are two adjacent first-order catchments, which consequently share the same lithological and climatic characteristics. The

climate is oceanic. Mean annual precipitation of the 1992–2002 period was 1161 mm (Ruiz et al., 2002; Legout et al., 2005). Mean annual temperature was 11.4°C (Ruiz et al., 2002). The bedrock belongs to the Paleozoic leucogranodiorite of Plomelin (Béchennec et al., 1999). The granite is fractured and fissured, and is overlaid by weathered material, with a mean thickness of about 20 m (Legchenko et al., 2004). The principal minerals in the granodiorite are quartz, plagioclase, K-feldspar, muscovite and biotite. Secondary minerals, such as clays (i.e. kaolinite and illite), are also present in the granitic arena.

Soils are mainly dystric cambisols developed on a granitic arena. Soils are well drained except in the relatively narrow bottomlands where hydromorphic soils are found. Land use is mainly agricultural (77%), with intensive cultivation of maize and grain and intensive grazing by dairy cows (Ruiz et al., 2002). The catchments were limed in 2002 and 2005.

The catchments are characterized by the presence of shallow groundwater developed perennially in the weathered granitic material, with the water table depth ranging from 2 to 8 m below the soil surface throughout the hydrological cycle.

4. Synopsis

4.1 Temporal and spatial variability of water quality at the catchment scale: Assessing long-term changes and hot spots of biogeochemical processes using the Isomap approach

The goal of Study 1 and Study 2 was to first identify the prevailing biogeochemical processes affecting water quality of catchment waters. Then, the long-term behavior of the prevailing biogeochemical processes in groundwater and stream water was determined using a low-pass filtering of time-series of component scores (Study 1). In contrast, Study 2 focused on the spatial variability of water quality by identifying hot spots of the prevailing biogeochemical processes at the catchment scale along different flow paths.

In the two studies, solute concentration data from wetland shallow groundwater, deep groundwater, and stream water (Study 1 and 2) as well as from soil solution of well drained soils (only Study 2) were merged, following the basic assumption that these different compartments form a continuum of flow paths and associated biogeochemical processes. In addition, it was assumed that a multitude of biogeochemical processes influences numerous chemical constituents in catchment waters. Thus, time series or spatial patterns of solute concentration likely reflect an interplay between different processes, and cannot be directly used to draw inferences about the identity and the intensity of single biogeochemical processes. Thus the Isometric Feature Mapping (Isomap) approach was used in both studies. It is a non-linear variant of the Principal Component Analysis (PCA). The basic idea of Principal Component Analysis is that due to correlations between different parameters in a

multivariate data set, a large fraction of the variance of the total data set can be represented by a small number of independent principal components.

Correlation of the component scores with the concentration of the different solutes was used to identify typical patterns that could be indicative for certain biogeochemical processes. Then the component scores could be used as a quantitative measure for the strength of the respective process. Correspondingly, time series and spatial patterns of the strength of these processes could be studied, and the rate of change of component scores along single flow paths could be used to identify regions with high process intensity.

Note that the terms “Isomap dimension”, “dimension scores” and “variable” in Study 2 are identical to the terms “Isomap component”, “component scores” and “parameter” in Study 1 and 3, respectively. For clarity, the latter terms are used in the following for all studies.

4.1.1 Long-term changes of biogeochemical processes (Study 1)

For assessing the long-term changes of biogeochemical processes, a data set of groundwater and stream water solute concentrations from the Lehstenbach and the Lysina catchment was used. As the catchments are comparable with respect to geology, land use, deposition history and climatic conditions, it was hypothesized that (non-linear) long-term patterns of single biogeochemical processes were similar. Short-term dynamics were abstracted from the time series of component scores at single sites and from meteorological data applying a low-pass filter.

Results of this study showed that a high fraction of the variance of the data set could be related to only four different biogeochemical processes. Dominant biogeochemical processes were similar in both catchments, despite lying 60 km apart from each other. However, the chemical composition of stream waters in the two catchments differ mainly due to different influences of redox and topsoil processes which could be related to the fraction of riparian wetlands in the respective catchments.

The Isomap approach allowed quantifying the effect of the different biogeochemical processes on single solutes. Moreover, the variation of solute concentration of single solutes could be ascribed to the interaction of different biogeochemical processes. For example, NO_3 and SO_4 concentrations showed an antagonism with each other in addition to their dependence on redox processes.

Long-term patterns of component scores were remarkably similar at different sites. However, the Lehstenbach and Lysina sampling sites could be split into three different groups. This grouping could be traced back to different damping with respect to depth that was likely due to the contrasting thickness of the regolith resulting in contrasting water flow paths in the two catchments.

The fraction of wetland area in the respective subcatchments as well as the varying thickness of the regolith turned out to control the different behaviors at different sites. Consequently, Study 3 focused on the interplay between biogeochemical and hydrological processes in a riparian wetland and on the

implications for stream water quality. As highlighted in Study 2, biogeochemical processes differ along different hydrological flow paths. Flow paths likely depend on the thickness of the regolith, which is directly related to weathering processes and weathering intensity. These processes are in turn influenced by anthropogenic impacts as could be shown in Study 4 and 5. Consequently, considering different flow paths and the complex interplay between hydrological, geochemical and anthropogenic processes is of crucial importance for understanding temporal patterns in water quality at the catchment scale.

4.1.2 Hot spots of biogeochemical processes at the catchment scale (Study 2)

In Study 2, we focused on spatial variability, namely on hot spots of biogeochemical processes at the catchment scale along different flow paths in the Lehstenbach catchment. For this purpose, soil solution, groundwater and stream water samples were taken, aimed at assessing the chemical evolution along different flow paths: flow paths from upslope soils to an upslope spring, from upslope soils to the catchment outlet, and wetland flow paths.

Based on the considerations concerning the relationship between specific solute concentrations and component scores discussed above, the following biogeochemical processes could be ascribed to the three components: (i) redox processes, (ii) acid-induced podsolization, and (iii) weathering processes. Podsolization as well as mineral weathering was likely enhanced by the acidifying effects of historical high sulfur deposition (Lischeid, 2001; Lischeid et al., 2004; Matzner et al., 2004), pointing to the interplay between biogeochemical and anthropogenic processes, as was investigated in detail in Study 4. Likewise, agricultural acidifying inputs (fertilizer application) leads to enhanced weathering processes as well, as was demonstrated in Study 5.

A change of Isomap component scores along the flow paths was assumed to indicate a change of the respective contribution of the biogeochemical transformation processes, resulting in a change of solute concentrations. Although the results do not allow direct inference of transformation rates of different processes, zones of major change of component scores on short distances likely represent the most reactive areas of the catchment, i.e. hot spots with respect to these processes.

A biogeochemical hot spot was identified in the uppermost 1 m soil layer with respect to acid-induced podsolization processes along the flow paths from upslope soils. Biogeochemical processes in deep groundwater had only minor effects on the biogeochemical turnover in catchment waters. Along wetland flow paths, biogeochemical hot spots were found in the first 10 cm with respect to redox processes and acid-induced podsolization, and in the uppermost 1 m soil layer with respect to weathering processes, respectively. These hot spots are assumed to account for a large fraction of biogeochemical turnover with respect to the different biogeochemical processes. Nearly 53% of the variance with respect to acid-induced podsolization could be traced back to the hot spot along the first 0.9 m of flow paths from upslope soils which represented only 2% of the total spatial volume of the

catchment. Nearly 67% and 44% of the variance with respect to redox processes and acid-induced podsolization could be traced back to the respective hot spots along wetland flow paths, representing only 0.1% of the total spatial volume of the catchment. In contrast, quantification was not possible for the hot spots of weathering processes, because of preferential sampling of the immobile fraction of the soil solution using soil suction cups instead of representing a continuum of the same flow path in different depth.

Besides the identification of hot spots along different flow paths, the results of the Isomap analysis were used to identify the predominating flow paths and biogeochemical processes crucial for the variability of surface water quality. Component scores differed substantially for different streams in the catchment, reflecting different contributing flow paths and biogeochemical processes which corresponded to the fraction of wetlands in the subcatchments. The highly dynamic pattern of component scores observed in the wetland stream water samples, indicating a high temporal variability of stream water chemistry, was investigated in detail in Study 3, elucidating the interplay between biogeochemical and hydrological processes.

The results of this study demonstrated that three predominating bundles of biogeochemical processes exhibited different patterns along subsurface flow paths. Up to 97% of the biogeochemical transformation of the chemical composition of soil solution, groundwater and stream water in the Lehstenbach catchment was restricted to less than 2% of the catchment's regolith, i.e., to the uppermost 0.1 or 0.9 m soil layer, pointing to a highly non-linear relationship between biogeochemical "active" areas and hydrological processes. The localization of biogeochemical hot spots within the catchment demonstrates on the one hand the spatial variability of biogeochemical processes within the catchment. On the other hand, hot spots are considered the most reactive areas of the catchment, i.e. zones of major change of solute concentrations within short distances, emphasizing that the chemical composition within single water components changes with respect to time and space. Compared to other studies which frequently described hot spots in terms of processes linked to the nitrogen or carbon cycle (McClain et al., 2003; Groffman et al., 2009a; Vidon et al., 2010; Andrews et al., 2011), this study considered 15 different solutes and electric conductivity and found clear effects of hot spots for all of these solutes. On the other hand, most solutes were affected by more than one of these three bundles of biogeochemical processes each with different hot spot patterns.

4.2 Temporal patterns of stream water quality traced back to interacting hydrological and biogeochemical processes in a riparian wetland (Study 3)

The uppermost soil layer in the wetland, where runoff of the wetland stream is mainly generated (Lischeid et al., 2002; Lischeid and Bittersohl, 2008), was identified to be a hot spot of biogeochemical processes and thus to play a major role for the biogeochemical transformation in the catchment as was demonstrated in Study 2. However, comprehensive studies in this wetland (Lischeid

et al., 2007; Fleckenstein et al., 2011; Knorr 2012) and in other riparian wetlands (Kerr et al., 2008; Vidon et al., 2014; Arnold et al., 2015) pointed to a complex interplay between biogeochemical and hydrological processes. Hydrologists aim to understand dynamics of runoff generation, ignoring the role of biogeochemical processes for solute export. In contrast, biogeochemists generally focus on understanding wetland internal processes, ignoring the role of hydrological boundary conditions for solute export from the wetland, except for changes in the water table depth. Thus, this study aimed at delineating and attaching weight to biogeochemical versus hydrological processes. To reach this aim, the temporal patterns of stream water chemistry were systematically traced back to different biogeochemical processes in the wetland, which were assumed to be related to the antecedent hydrological boundary conditions in the wetland. Thus, a subset of data from Study 2 from a small wetland stream was used for a subsequent Cluster Analysis, in order to group water samples that were influenced by the same biogeochemical processes and thus showed a similar chemical composition. It was hypothesized that the different clusters of stream water samples represented the different antecedent hydrological and biogeochemical conditions in the wetland controlling stream water chemistry.

Four clusters have been determined, which differed significantly with respect to the scores of the Isomap components, and with respect to most of the solutes as well, indicating that the different clusters represent different types of hydrochemical states of the wetland stream. In general, assignment to clusters exhibited considerable persistency, without systematic change of cluster occurrence before, during or after runoff events being observed. Thus, pronounced changes of stream water solute concentration can in the first place be ascribed to slowly modifying conditions within the wetland, i.e. wetland internal processes, rather than due to short-term hydrological processes. Time series of assignment to clusters roughly followed a seasonal pattern, albeit with considerable modification within and between the years. Groundwater level, water residence time and air temperature governing microbial activity in the wetland turned out to be the main factors controlling cluster occurrence. Stream water chemistry changed substantially for up to 28 days or longer after periods of extensive groundwater level drawdown (more than 20 cm), due to flushing of solutes like NO_3 or SO_4 that accumulated during the drought period. Obviously memory effects have to be taken into account here. Thus, extensive drought periods that are expected to occur more frequently due to climate change, seem to generate a high NO_3 and SO_4 export from the wetland to the Moorbach stream, emphasizing the non-linear interplay between biogeochemical and hydrological processes in the wetland. Likewise, DOC dynamics in stream water was not controlled by near-surface runoff (Hornberger et al., 1994; Hagedorn et al., 2000; Mitchell et al., 2006; Inamdar et al. 2008) in the layer of highest DOC production (Cole et al., 2002), but was dependent on redox reactions which were controlled by the water table depth and thus the antecedent moisture conditions in the wetland, as pointed out for pore waters in the riparian wetland by Knorr (2012). Thus, the interplay between the hydrological boundary

conditions and the biogeochemical processes governed by the season via the microbial activity in the wetland turned out to determine the different types of Moorbach stream water quality.

To conclude, biological activity in the riparian wetland, interacting with water table dynamics, proved to be a primary determinant of stream water quality and solute export. Temporal variability of stream water quality during single runoff events was negligible. More than a shift of annual mean values, single dry and warm periods are likely to predominate the dynamics and thus limit the retention capacity of wetlands and enhance solute export to the streams. The results of this study confirm the basic assumption of non-linear interactions between catchment processes, which render understanding and prediction of long-term behavior of stream water quality difficult. However, a sound understanding of these dynamics is a necessary prerequisite for assessing the impact of climate and land use change on stream water quality, nutrient export, and carbon sequestration in riparian wetlands.

4.3 Water quality influenced by weathering processes enhanced by anthropogenic impacts

Weathering processes are crucial for the buffering of acidifying inputs in catchments (Koseva et al., 2010; Fortner et al., 2012; Huang et al., 2013; Takaya, 2014). In Study 2, cation exchange and silicate weathering processes have been identified as predominating processes affecting the quality of catchment waters. It was pointed out that these processes were enhanced by historical acid atmospheric inputs in the catchment. Similarly, in agricultural areas, the application of physiological acid fertilizers and nitrogen fertilizers in the form of ammonia may enhance the cation leaching through the soil profile into ground and surface waters (Fortner et al., 2012; Meng et al., 2014). However, the role of different minerals in base cation release is controversially discussed in literature. Consequently, in the third part of this thesis, the mineralogical sources of (i) the groundwater's buffer capacity against acid atmospheric deposition (Study 4) and of (ii) the high cation loads in surface waters induced by intensive agricultural activities (Study 5) were determined. The forested Lehstenbach catchment in Study 4 and the agricultural Kerrien and Kerbernez catchments in Study 5 exhibit a comparable geology but differ with respect to land use and thus the degree of anthropogenic impact. It was hypothesized that the catchments differ with respect to the effects of anthropogenic impact on weathering processes which can be used to evaluate the interaction between anthropogenic and geochemical processes in the catchments.

In both studies, $^{87}Sr/^{86}Sr$ ratios and major and trace elements were analyzed. Strontium isotopes and major and trace elements are used to identify hydrological and hydrogeochemical processes in watersheds (Bullen and Kendall, 1998; Négrel et al., 2007; Mavris et al., 2010; Andrews et al., 2016) as well as to discriminate between natural and anthropogenic element sources in catchments (Böhlke and Horan, 2000; Nakano et al., 2008; Potot et al., 2012, Shin et al., 2017). A summary concerning the methodology of Sr isotopes in general, and the use of Sr isotopes to identify hydrological and hydrogeochemical processes in watersheds, is given e.g. in Bullen and Kendall (1998).

Bearing in mind the following considerations, strontium isotopes and chemical element ratios were interpreted. Three sources of Sr^{2+} and major cations to soil- and groundwater are possible: mineral weathering, atmospheric deposition, and additional material applied on soil, such as lime or fertilizers. The different cations can be released either into the groundwater or into the soil mobile water and leave the soil, or can constitute a reservoir with an intermediate mobility in the clay fraction (cation exchange pool).

4.3.1 Mineralogical sources of the buffer capacity against acid atmospheric deposition (Study 4)

In this study, the goal was to ascertain the mineralogical sources of the groundwater's buffer capacity against acid atmospheric deposition in the forested Lehstenbach catchment. $^{87}Sr/^{86}Sr$ ratios and major and trace elements were determined in whole rock leachates, separated minerals and groundwater, soil water and stream water samples to identify the weathering sequence of the granite bedrock. Mineralogical sources were constrained using element concentration ratios, Keeling diagrams, and a PCA. It was assumed that the water samples represented varying fractions of single endmembers which were determined using the PCA. Saturation indices were calculated for all samples from groundwater outside the wetlands with respect to biotite, feldspars and apatite.

Biotite and apatite were identified as endmembers, in contrast to plagioclase and K-feldspar, although they are the prevailing minerals in the granite of the Lehstenbach catchment in addition to quartz. However, preferential cation release from plagioclase and feldspar is likely, indicating that plagioclase and feldspars certainly contribute to the buffer capacity of groundwater, albeit to unknown degrees. Apatite dissolution, preferential cation release from feldspars and biotite, and feldspars weathering was determined as the weathering sequence of the Lehstenbach granite. These results showed that the release of base cations via weathering apparently was not proportional to the fraction of each mineral in the bedrock, pointing to a non-linear behavior of weathering processes. Preferential cation release from plagioclase and feldspars as well as apatite dissolution in an early phase of weathering could be considered as a hot spot of cation release at the small scale. In contrast, in Study 2, hot spots of biogeochemical processes, including weathering processes, controlling catchment water chemistry were identified at the catchment scale. These results demonstrate (i) that weathering processes vary from the small scale to the catchment scale, and (ii) that processes at the small scale can considerably influence water chemistry at the catchment scale.

Water samples taken mainly from 0.9 m depth or deeper were used to determine the weathering sequence in Study 4. In contrast, the hot spot of weathering processes at the catchment scale has been identified in the uppermost 1 m soil layer at upslope and wetland sites in Study 2, representing the biogeochemically most active zone. The weathering front propagates with depth, so that soil layers at the surface are more weathered than soil layers in greater depth, which shows a less intense signal of

weathering processes. Thus, determining the weathering sequence based on water samples taken from 0.9 m depth will primarily consider the early stages of weathering and ignore later stages.

Additional processes and base cation sources (e.g. liming) influencing the chemical composition of catchment waters beside weathering, i.e. biogeochemical processes like plant-uptake, element cycling and temporary ion-exchange processes were considered to play a negligible role for groundwater at more than 1 m depth. Indeed, 97% of the biogeochemical transformation of the chemical composition of soil solution, groundwater and stream water turned out to be restricted to the uppermost 1 m soil layer in Study 2. Thus, water samples from deeper soil have passed the biogeochemically most active zone, enabling the investigation of weathering processes without the additional substantial influence of other biogeochemical processes on water chemistry. However, contamination by filter gravel in groundwater was observed in some wells, which was in line with the results in Study 2, showing that drilling of groundwater wells can change groundwater chemistry over a long period of time. Similar findings were reported by Neal et al. (1997b).

Overall, apatite dissolution and preferential cation release from plagioclase and feldspars in an initial phase of weathering, as well as plagioclase, feldspar and biotite weathering was found to control base cation release in the catchment under study. Base cation input by weathering processes to groundwater buffer capacity by far exceeded that of atmospheric deposition and liming. Accessory minerals like apatite, comprising less than 0.5% of the total volume of the rock, turned out to play a major role for base cation release, emphasizing highly non-linear relationships between mineral abundance and cation release. Hot spots at the small scale, like apatite dissolution or preferential cation release from plagioclase and feldspars, can have substantial effects on water chemistry at the catchment scale.

4.3.2 Weathering processes induced by intensive agricultural activities (Study 5)

The application of physiological acid fertilizers may enhance cation leaching through the soil profile into ground- and surface waters. Thus, in the Kerrien and Kerbernez catchments which are characterized by intensive agriculture, base cation sources have been studied using chemical element and Sr isotopic ratios of precipitations, soil water- and NH_4 acetate-leachates, soil bulk digestion, separated minerals, and stream water samples. The relative contribution of Sr from soil weathering and fertilizers to waters was calculated using mass balance equations with respect to different endmembers (separated minerals, animal manures) and for different ‘water’ mixture components, i.e. waters, H_2O-leachates or NH_4 acetate-leachates.

Manure contribution predominated cation sources in the topsoil (0-20 cm). Manure, plagioclase and biotite controlled effects of alteration in the mid-soils (20-70 cm). Biotite weathering occurred in the deeper soil horizons and in the saprolite itself, and may be enhanced by acidification due to the use of fertilizers. Accordingly, mainly anthropogenic processes controlled cation sources in the upper soil layers. With increasing depth, the direct influence of anthropogenic processes decreased in favor of

weathering processes, which in turn were enhanced by anthropogenic acid inputs. Acidification due to the use of fertilizers led to extremely high dissolved cation concentrations in stream waters, comparable to those encountered in tropical environments where chemical weathering rates are extremely pronounced (Oliva et al., 2003; White and Blum, 1995; Thomas et al., 2014). Stream water chemistry was different from soil water, with a large part of base cations in stream waters originating from enhanced silicate weathering (plagioclase and biotite dissolution) in the different soil layers, and in the saprolite, instead of originating from the application of fertilizers itself. In contrast, anthropogenically controlled soil waters only played a minor role for stream water chemistry. Thus, stream water chemistry was not directly but indirectly influenced by agricultural impacts. Soil acidification induced by agriculture allows the mobilization of cations stored in soil layers, enhances the rock weathering, and accelerates plagioclase dissolution, pointing to considerable interaction between anthropogenic and geochemical processes which can highly influence stream water quality. In the long-term, it could be assumed that an increased thickness of the regolith, due to enhanced weathering processes, will change hydrological flow paths and thus the role of different biogeochemical processes for catchment water chemistry, as was pointed out in Study 1. Consequently, intensive agriculture will change biogeochemical processes in the short term and in the long-term due to intensifying weathering processes.

Major cation sources and the identified weathering sequence in the Kerrien and Kerbernez catchments could be compared to those found in the forested Lehstenbach catchment in order to evaluate the different effects of anthropogenic inputs on catchment water chemistry as was summarized in Table 1. In all catchments, cation sources in the topsoil were controlled by the respective anthropogenic influence, i.e. an atmospheric deposition signature and an Al saturation of more than 97% of the cation exchange capacity in the mineral soil of the Lehstenbach catchment (Gerstberger et al., 2004), and a dominant manure signature in the Kerrien and Kerbernez catchments. Soil acidification due to acid atmospheric deposition (high sulfur deposition) and fertilizer application leads to enhanced mineral weathering, cation mobilization in soil layers, higher cation loads in stream water and cation deficiency for trees in the forested catchment (Alewell et al. 2000), or likely to a decrease of agricultural productivity in the agricultural catchments. Weathering processes in the subsoil can be enhanced by acidification and can thus play a major role for base cation supply. This was particularly pronounced in the Kerrien and Kerbernez catchments, where cation loads in stream waters were comparable to those in tropical environments with extremely high chemical weathering rates. Furthermore, apatite dissolution contributed to base cation supply in an early phase of weathering in the forested Lehstenbach catchment. In contrast, in the agricultural Kerrien and Kerbernez catchments, apatite presumably has been dissolved and exported from the catchment due to enhanced weathering processes. This points to a higher intensification of weathering processes due to fertilizer application compared to acid atmospheric deposition inputs, although the controlling processes, cation sources, and the implications for catchment functioning were comparable.

Tab. 1: Comparison between anthropogenic inputs, mineral weathering sequence, and implications for catchment processes for the forested Lehstenbach catchment and the Kerrien and Kerbernez catchments.

	Lehstenbach catchment	**Kerrien/Kerbernez catchment**
Anthropogenic inputs	Acid atmospheric deposition (high sulfur deposition) in the past	Application of chemical and organic fertilizer (pig slurry, cattle manure)
Mineral weathering sequence	Contribution from trace mineral dissolution (apatite) and preferential cation release from plagioclase and feldspars identified, i.e. initial stage of weathering identified (sampling in > 90 cm depth) biotite dissolution, plagioclase and feldspar dissolution (Study 4) weathering of Al containing clay minerals (Study 2)	No contribution from trace mineral dissolution (apatite), i.e. apatite likely dissolved in soil layers under study (< 120 cm depth), presumably by enhanced weathering processes due to soil acidification biotite dissolution plagioclase dissolution K-feldspar and muscovite dissolution
Implications for catchment processes	Al saturation of more than 97% of the cation exchange capacity (Gerstberger et al., 2004) Enhanced mineral weathering in the deeper soil layers due to acidifying effects of high historical sulfur deposition (cf. Study 2) Enhanced cation export to streams (Lischeid et al., 2004) Cation deficiency for trees (Alewell et al., 2000)	Predomination of manure contribution in the topsoil Even more enhanced mineral weathering due to fertilizer application leading to soil acidification and mobilization of cations stored in soil layers (cation loss) High cation export to streams (comparable to those in tropical environments with high chemical weathering rates) soil destabilization agricultural productivity decrease
Conclusions	Influence of weathering processes increases with depth; weathering processes in the subsoil enhanced due to anthropogenic inputs Interaction between anthropogenic processes and weathering processes Change of water flow paths in the long-term due to enhanced weathering	

	processes and increased thickness of the regolith is likely, i.e. interaction between hydrological and weathering processes Comparable controlling processes, cation sources, and implications for catchment functioning, but higher intensification of weathering processes in intensive agricultural catchments compared to forested catchments with acid atmospheric deposition

5. Conclusions

5.1 Water quality at the catchment scale as the result of non-linear interactions between predominating catchment processes

A small number of dominant biogeochemical processes influencing the temporal and spatial variability of water chemistry in catchments could be identified using the non-linear Isomap approach. Dominant processes were comparable at non-adjacent sites but with comparable geology and land-use. The results of this study enabled the identification of hot spots of biogeochemical processes at the catchment scale. Numerous biogeochemical, hydrological, and anthropogenic processes were found to interact with each other, mostly with non-linear patterns. Figure 6 gives a synthetic overview of the results of this thesis.

For achieving a better understanding of the complex interplay between geochemical, biological, hydrological, and anthropogenic processes, the identification of dominant processes in the catchment was a necessary prerequisite. As non-linear relationships are common in ecological data, the non-linear Isomap approach was used in Study 1 and Study 2. Compared to linear methods of dimensionality reduction, Isomap allowed to map both linear and non-linear relationships and did not need any a priori assumptions in order to project the data (Böttcher et al., 2014). However, to be able to draw the right conclusions from multivariate statistical approaches such as Isomap, it was necessary to possess a basic knowledge of the structure of the system and of the processes that may occur (Maassen et al. 2012). This was the case for the two granitic catchments under study.

Most of the biogeochemical transformation in the catchment is located in the first meter of flow paths from upslope sites, as well as at the wetland sites, and could be considered as hot spots of biogeochemical processes at the catchment scale (Study 2, Fig. 6). Processes in this very small fraction of the catchment have a high influence on catchment water chemistry, demonstrating a highly non-linear relationship between the “active volume” of the catchment and the fraction of biogeochemical transformation. A high anthropogenic signature in the soil solution and in the cation exchange complex, i.e. in the “active volume” of the catchment, was found (Study 2 and Study 5), emphasizing the importance of anthropogenic processes for catchment water quality.

Biogeochemical processes in the regolith and in deep groundwater had only minor effects on the biogeochemical turnover in catchment waters in the forested Lehstenbach catchment (Study 2).

However, weathering processes and solute export were enhanced by anthropogenic processes (acid atmospheric deposition, application of mineral and organic fertilizer) as was demonstrated in Study 4 and Study 5, emphasizing the interplay between anthropogenic and weathering processes (Fig. 6). In turn, intensified weathering likely leads to an increased thickness of the regolith and will change hydrological flow paths in the long-term, emphasizing the interplay between geochemical, anthropogenic and hydrological processes (Fig. 6). Hot spots at the small scale, i.e. trace mineral dissolution and preferential cation release from feldspars, were found to play a major role in base cation release in groundwater and in water chemistry at the catchment scale (Study 4, Fig. 6).

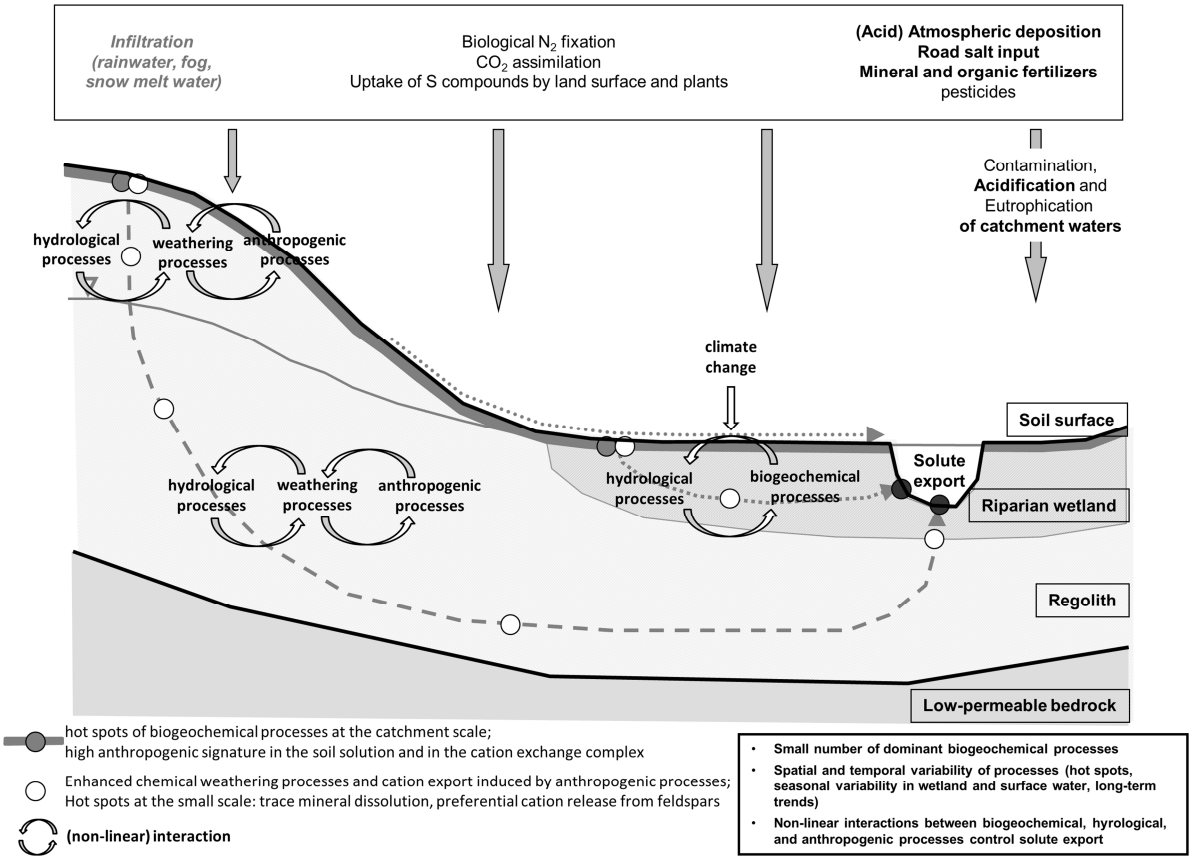

Fig. 6: Synthetic overview of identified hot spots and interacting biogeochemical, anthropogenic and hydrological processes influencing water quality in forested and agricultural granitic catchments. Bold: predominating (anthropogenic) element sources and processes. Identified dominant biogeochemical processes were redox processes, topsoil processes, acid-induced podsolization, weathering processes, road salt input, and SO_4 contamination. Hot spots at the catchment scale were found with respect to redox processes, acid-induced podsolization processes and weathering processes, respectively.

Weathering processes and base cation sources were investigated using element ratios and Keeling diagrams. In fact, only the combination between isotope techniques and major and trace element ratios allowed to discriminate between different base cation sources like deposition, geogenic origin, and anthropogenic sources, and thus identify the weathering sequence in the Lehstenbach catchment and of the cation sources of the high cation loads in the Kerrien and Kerbernez catchments. A necessary prerequisite for using Sr isotopes to trace mixing phenomena and water-rock interactions in the aquifer

is the fact that Sr isotopes will not fractionate through natural processes due to the low mass contrast between the ^{87}Sr and ^{86}Sr isotopes (Widory et al. 2004).

A considerable interplay between hydrological and biogeochemical processes in the wetland, i.e. biological activity and changing water table dynamics which was influenced by global climate change, turned out to be crucial for stream water quality and solute export (Study 3, Fig. 6.). Thus, the latter were controlled by internal wetland processes rather than by short-term hydrological processes. Different hydrochemical states of the wetland stream were identified using cluster analysis on a subset of the Isomap analysis data. In general, clustering overemphasizes differences between clusters whereas the variability within the clusters is disregarded. Assigning single samples from a more or less continuous data set to a certain cluster is, to a certain degree, always arbitrary and can be questioned. However, in large data sets, like that used in this thesis, clustering helps detect similarities between samples and thus identify intrinsic structures. Applied together with the non-linear Isomap analysis, relationships among different water chemical species could be explained, suggesting hydrochemical processes and defining hydrochemical facies important to water chemistry evolution.

In general, catchment water chemistry, and thus solute export both in the short-term and the long-term, was influenced by the non-linear interplay between biogeochemical processes, including weathering processes, hydrological and anthropogenic processes (acidifying inputs, global climate change). Using a combination of various types of data, and of various methods using field data helped to achieve a better understanding of the inherent complexity of the interactions between catchment processes and factors of influence on water quality at the catchment scale.

Anthropogenic impacts on water quality in catchments are of special interest for water resources management that aims at reaching the ‘good ecological state’ for all waters in Europe (EU Water Framework Directive). The results of this thesis showed that elemental input from anthropogenic sources like acid atmospheric deposition, road salt input and mineral and organic fertilizers turned out to play a major role for catchment water chemistry, as compared to natural element sources like biological N_2 fixation, CO_2 assimilation or uptake of S compounds by land surface and plants (Fig. 6). Anthropogenic processes highly interacted with “natural” processes, often in a non-linear and indirect way, thus changing catchment water chemistry. Processes like sulfate contamination, acid-induced podsolization and road salt application were found to be predominating processes influencing water quality in the forested catchments under study, despite a significant reduction of acid atmospheric deposition in the last 20 years (Matzner et al., 2004) and road salt application only in a restricted area in the catchment. Soil acidification induced by agriculture leads to large cation export due to enhanced weathering and should be considered in term as a potential mechanism for soil destabilization and agricultural productivity decrease. Finally, climate change will enhance solute export to the streams. More than a shift of annual mean values, single dry and warm periods are likely to predominate the dynamics and thus limit the retention capacity of wetlands leading to higher nutrient loads in adjacent ecosystems, at least episodically.

5.2 General conclusions and further investigations

Water resources management has to consider spatial and temporal patterns of biogeochemical processes and anthropogenic impacts. Management practices are often based on results from biogeochemical modelling. The integral approach used in this thesis helps focus on the predominating biogeochemical processes and on biogeochemical hot spots with respect to these processes, and distinguish between short-term and long-term shifts. Thus, the number of processes included in modelling approaches can be reduced, and spatial and temporal patterns can be included where necessary and appropriate.

A sound understanding of the interplay between hydrological and biogeochemical processes in catchments is a necessary prerequisite for assessing the impact of climate and land use change on groundwater and surface water quality, as well as nutrient and carbon dynamics in terrestrial ecosystems. However, non-linear interactions between biogeochemical, anthropogenic and hydrological processes render the understanding and prediction of long-term behavior of catchment water quality difficult. Thus, the systematic identification and characterization of hot spots and of hot moments is of great interest. Whereas biogeochemical hot spots were investigated in this thesis, further investigations are needed for identifying and characterizing biogeochemical hot moments in the catchment.

As single processes like the weathering of trace minerals can have a significant influence on catchment water chemistry, knowing single processes in the catchment under study is of great concern. Consequently, research on single processes in the different environmental disciplines is a necessary prerequisite for understanding and predicting of temporal and spatial patterns of catchment water chemistry. However, due to the dynamic interactions between the different processes in catchments, knowledge about single processes in the catchment has to be merged within an integral approach like that used in this thesis. Such an integral approach will naturally be an interdisciplinary approach, integrating contributions from different environmental science disciplines, like biogeochemistry, microbiology and hydrology. Thus, further research aiming at understanding and predicting temporal and spatial dynamics of catchment water chemistry should favor interdisciplinary approaches.

In this thesis, water chemical data of a frequency not exceeding daily measurements were used. However, the time scale of hydrological processes is often on the order of minutes or hours. High-frequency measurements of chemical data showed that much of the information in water chemistry is lost even with daily measurements (Kirchner et al., 2004). It is likely that chemical measurements at the same time-scale than that of hydrological data, i.e. high-frequency measurements at the time scale of minutes or hours, will give information about the linkage between biogeochemical and hydrological processes in the catchment and thus improve the understanding of spatial and temporal patterns of catchment water chemistry (e.g. von Freyberg et al., 2017).

The results of this thesis were based on granitic catchments. Comparable results of the predominating biogeochemical processes are expected for other catchments with comparable geology, land use, climate, and acid deposition history. However, results will differ for catchments with other geology, land use, climate, and anthropogenic impact as each factor or process can change the biogeochemical and hydrological functioning of the system. Thus, contrasting catchments have to be investigated separately.

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List of manuscripts and specification of own contributions

This thesis consists of five published manuscripts. The list below details the contributions of all co-authors.

Study 1

Authors	G. Lischeid, P. Krám, C. Weyer
Title	Tracing biogeochemical processes in small catchments using non-linear methods
Status	published
Textbook	Müller et al. (Eds.): Long-Term Ecological Research, Springer Science + Business Media B.V.

Contributions

Lischeid	90%	idea, methods, data collection, data analysis, manuscript writing, figures, discussion, editing, corresponding author
Krám	5%	data collection and discussion
Weyer	5%	data collection and discussion

Study 2

Authors	C. Weyer, S. Peiffer, K. Schulze, W. Borken, G. Lischeid
Title	Catchments as heterogeneous and multi-species reactors: An integral approach for identifying biogeochemical hot-spots at the catchment scale
Status	published
Journal	Journal of Hydrology

Contributions

Weyer	60%	idea, methods, data collection, laboratory work, data analysis, manuscript writing, figures, discussion, editing, corresponding author
Peiffer	15%	idea, discussion, editing
Schulze	5%	data collection and discussion
Borken	5%	data collection and discussion
Lischeid	15%	idea, discussion, editing

Study 3

Authors	C. Weyer, S. Peiffer, G. Lischeid
Title	Stream water quality affected by interacting hydrological and biogeochemical processes in a riparian wetland
Status	published

Journal	Journal of Hydrology		
Contributions			
	Weyer	70%	idea, methods, data collection, laboratory work, data analysis, manuscript writing, figures, discussion, editing, corresponding author
	Peiffer	15%	idea, discussion, editing
	Lischeid	15%	idea, discussion, editing

Study 4

Authors	C. Weyer, G. Lischeid, L. Aquilina, A.-C. Pierson-Wickmann, C. Martin		
Title	Mineralogical sources of the buffer capacity in a granite catchment determined by strontium isotopes		
Status	published		
Journal	Applied Geochemistry		
Contributions			
	Weyer	70%	idea, methods, data collection, laboratory work, data analysis, manuscript writing, figures, discussion, editing, corresponding author
	Lischeid	15%	idea, data collection, discussion, editing
	Aquilina	5%	idea, discussion
	Pierson-Wickmann	5%	discussion
	Martin	5%	discussion

Study 5

Authors	A.-C. Pierson-Wickmann, L. Aquilina, C. Weyer, J. Molénat, G. Lischeid		
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	Pierson-Wickmann	70%	idea, methods, data collection, laboratory work, data analysis, manuscript writing, figures, discussion, editing, corresponding author
	Aquilina	5%	idea, discussion
	Weyer	15%	data collection, laboratory work, discussion
	Molénat	5%	discussion
	Lischeid	5%	discussion

Erratum

Study 2, Weyer et al. 2014

- Chapter 5.1.1, line 16: “Mn” is missing in the sentence: “The high correlation of **Mn** with the 1st dimension has to be interpreted with caution.”

Study 4, Weyer et al. 2008

- Fig. 6: explanation of the symbols ✳, +, × in the figure is missing in the legend: × rock leachates of P17 and P20 3-4 m depth; + rock leachates of P17 and P20 6-7 m depth, ✳ rock leachates of P17 and P20 9-10 m depth
- Fig. 7: “Loadings of the parameters used for the PCA on the ***two*** principal components (pc)” instead of: “Loadings of the parameters used for the PCA on the three principal components (pc)”
- Chapter 5.2.1, line 3 and 4: “Liming was ***not*** performed in the wetlands to avoid enhanced mineralization of the peat.” instead of: “Liming was performed in the wetlands to avoid enhanced mineralization of the peat.”

Study 5, Pierson-Wickmann et al. 2009

- Fig. 3 and Fig. 4: The text of Fig. 3 was interchanged with the text of Fig. 4.
- Chapter 4.1.2.2., end of the 4th paragraph: “(A, B, C and D in Fig. 4a)” instead of “(A, B, C and D in Fig. 3a)”.
- Chapter 5.1, 2nd paragraph, line 8: the citation of “Weyer et al., 2008” is not correct

Study 1

Tracing biogeochemical processes in small catchments using non-linear methods

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Abstract

Since the 1980s a variety of biogeochemical catchments studies have been set up to investigate the cycling of water and solutes. Groundwater and streams have been sampled to investigate the dominant processes of solute turnover in the subsoil and to monitor their long-term changes. Usually a variety of processes interact, partly in a highly non-linear manner. Consequently, identifing the dominant processes is not an easy task. In this study, a non-linear variant of the principal component analysis was used to identify the dominant processes in groundwater and streamwater of two forested catchments in the East Bavarian-West Bohemian crystalline basement. The catchments are approximately 60 km apart, but exhibit similar bedrock, soils, climate, land use and atmospheric deposition history. Both have been monitored since the end of the 1980s until today, that is, during a

period of dramatic decrease of atmospheric deposition of sulfur and accompanying base cations. Time series of component scores at different sites were investigated. Non-linear long-term trends were determined using a low-pass filter based on a Lomb-Scargle spectrum analysis.

The first four components accounted for 94% of the variance of the data set. The component scores could be interpreted as quantitative measures of biogeochemical processes. Among these, redox processes played a dominant role even in apparently oxic parts of the aquifers. Low-pass filtered time series of the component scores showed consistent, although mostly non-linear trends in both catchments.

Keywords: Groundwater quality; streamwater quality; Isometric Feature Mapping; non-linearity; time series analysis; trend analysis

1. Introduction

Water resources management requires sound knowledge of the dominant hydrological and biogeochemical processes that affect water availability and water quality. Based on a multitude of process studies both in the laboratory and in the field, it is known that often many processes interact in a non-linear way and via feed-back loops that make the determination of dominant processes at large scales difficult. Natural sources of spatial and temporal variability, like heterogeneity of soil properties or interannual climatic variability have to be differentiated from anthropogenic impacts and effects of long-term climate change. In addition, small-scale effects have to be distinguished from more general patterns that are typical for large regions.

Environmental monitoring aims at assessing spatial or temporal patterns of single parameters, like concentration of solutes or abundance of species. In many cases of natural resources management, however, data about observed parameters are used to infer what and to what degree different processes had an impact on the system in order to evaluate single measures and to decide about further management strategies. To that end, environmental monitoring often focuses on single indicator parameters that are assumed to be very closely related to single processes. That approach might work fine in some cases, but is clearly limited to certain boundary conditions.

In this study a different approach is followed for analyzing long-term water quality data. Firstly, a joint analysis of groundwater and surface water is performed. Although a couple of processes are restricted to either groundwater or surface water systems, it is assumed that the most dominating processes are the same. However, it is taken into account that the extent to what these processes affect solute concentration differs between the two systems as well as they vary in space and time. Secondly, it is assumed that every single process alters solute concentration in a typical way. That can be used to determine these processes by a variant of a principal component analysis. If principal components can

be ascribed to single biogeochemical processes, the scores of the components can be interpreted as quantitative measures of these processes. Then, time series of the component scores can be analyzed.

Thirdly, relationships between different solutes in groundwater and streamwater systems are often non-linear. This fact is accounted for by using a non-linear version of the principal component analysis. Fourthly, the long-term development of natural processes is very unlikely to follow a linear trend. On the other hand, the short-term variability of natural processes requires filtering the long-term components. In this study, a low-pass filter is applied based on a spectral analysis of the time series of components.

To summarize, the objective of this study was to identify the prevailing biogeochemical processes that affect groundwater and stream water quality in two similar forested catchments at numerous site, to investigate spatial patterns of processes, and to determine the long-term behaviour with respect to these processes.

2. Data

The data set comprises groundwater and streamwater solute concentration data from the sub-mountainous region of the crystalline basement along the German-Czech border. Here, extensive biogeochemical monitoring programs have been run since the end of the 1980s in two catchments that are assumed to represent typical conditions in this region. In both catchments the bedrock consists of granite, overlain by dystric cambisols and podzols. Fibric histosols and dystric gleysols predominate in the extended riparian zones. A dense network of natural streams and artificial channels exists in both catchments. Landuse is forestry exclusively, consisting of Norway spruce (*Picea abies* (L.) Karst.) stands.

The catchments are located at about 60 km distance. The Lysina catchment is part of the Slavkovský les in the Czech Republic, at 50°03' N and 12°40' E. The Lehstenbach catchment belongs to the Fichtelgebirge region in Germany and is located at 50°08' N and 11°52' E. The catchment area is 0.273 km^2 at Lysina, and 4.2 km^2 at Lehstenbach. Elevation ranges between 829 and 949 m a.s.l. at Lysina, and between 695 and 877 m a.s.l. at Lehstenbach. The thickness of the regolith is about 2.5 m in the Lysina catchment, and up to 40 m in the Lehstenbach catchment.

Annual mean precipitation of the 1991-2001 period was 933 mm at Lysina and 985 mm at Lehstenbach. Annual mean runoff was 432 mm and 470 mm, respectively. Annual mean air temperature is about 5.2°C at Lysina, and 5 - 6.5°C in the Lehstenbach catchment, depending on altitude. Snowpack usually develops in December or January and final snowmelt occurs in March or April.

An extensive monitoring program has been performed at both sites since the end of the 1980s (Krám et al. 1997, Matzner 2004). Both sites have been severely impacted by nitrogen and sulfate deposition.

Sulfate deposition peaked in the 1970s and decreased by more than 80% since then at both sites (Hruška et al. 2002, Matzner et al. 2004, EMEP 2007). In contrast, neither nitrogen deposition nor nitrogen concentration in the streams exhibited any clear trend at Lehstenbach. At Lysina, nitrogen deposition 1998–2000 was only 73% of that in 1991-1993 (Hruška et al. 2002), and the nitrate peaks in the winter season started to decrease in the end of the 1990s. Besides, there was no change of land use or extended clear-felling. However, the upslope parts of the Lehstenbach catchment have been limed several times.

Tab. 1: Overview over the data sets used in this study.

Component	Catchment	Number of sites	Period	Number of samples
Shallow groundwater (0.9 m – 4.5 m)	Lehstenbach:	6	2001-2004	212
	Lysina:	7	2000	82
Deep groundwater (1 m – 24 m)	Lehstenbach:	6	1988-2007	606
	Lysina:	-	-	-
Upslope springs	Lehstenbach:	1	1988-2006	403
	Lysina:	1	1989-2007	214
Streams	Lehstenbach:	4	1987-2007	1157
	Lysina:	2	1989-2007	1382
In total		**27**	**1987-2007**	**4056**

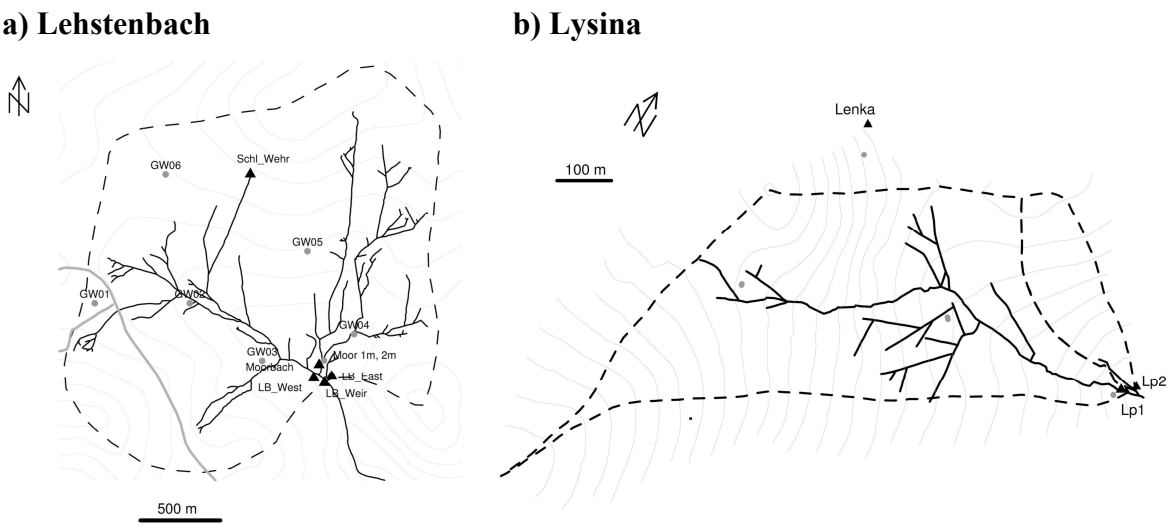

Fig. 1: Map of the Lysina and Lehstenbach catchments. Solid black lines denote streams, grey lines contour lines at 20 m (Lehstenbach) or 10 m interval (Lysina), dashed black lines the catchment boundaries, bold grey lines public roads. Groundwater wells are given by grey dots, spring and stream water sampling sites by black triangles.

In total, the data set used for this analysis comprises 13 parameters of more than 4000 samples. Samples were taken from 1987 throughout 2007 at 27 different sites in the two catchments (Tab. 1). The location of the sampling sites is given in Fig. 1. The parameters comprise Al, Ca, Cl^-, DOC, Fe, K, Mg, Mn, Na, NO_3^-, Si, and SO_4^{2-} and pH values. Streamwater samples had been taken as grab samples. Groundwater samples had been taken by a submersed pump and by a vacuum pump in the Lysina groundwater wells. Part of the Lehstenbach data was kindly provided by the Bavarian Environmental Agency which is highly appreciated. Quality assurance of the data was performed prior to this study by the Czech Geological Survey (Lysina data), the BayCEER central laboratory and the Bavarian Environmental Agency (Lehstenbach data).

If any long-term trends were to be found in the water quality data, it should be tested whether they were related to trends of meteorological parameters. To that end, time series of daily precipitation and air temperature data were included into the analysis. At Lehstenbach precipitation and air temperature have been measured at an open field site in the catchment. For Lysina, precipitation data from Kladská (at 1 km distance) and Lazy (at 5 km distance) and temperature data from Mariánská Lázně (at 8 km distance) were available. In addition, data from the Braunersgrün meteorological station of the Bavarian Agency for Agriculture were used. Braunersgrün is located between the two catchments, 18 km east of Lehstenbach and 44 km west of Lysina, although at lower altitude (590 m abs.). The data were downloaded at http://www.lfl.bayern.de. In this analysis, long-term shifts of meteorological parameters were investigated rather than absolute values. Thus, neither precipitation nor temperature data were corrected to account for different altitude or exposition.

3. Methods

Values less than the limit of quantization were replaced by 0.5 times that limit. Missing values were replaced by the mean of the respective parameter. The data were normalized to zero mean and unit variance for each parameter separately. All statistical analyses were performed using the R statistical software environment (R Development Core Team 2006).

3.1 Principal Component Analysis

The basic idea of principal component analysis is that due to correlations between different parameters in a multivariate data set, a large fraction of the variance of the total data set can be represented by a small number of principal components. There are different ways how to determine these low-dimensional components.

Linear Principal Component Analysis

The linear principal component analysis (PCA) is based on an eigenvalue decomposition of the covariance matrix. In case of z-normalized data, the covariance is equal to the Pearson correlation. The eigenvectors form the independent axes. These axes are usually interpreted based on their correlations with single parameters of the data set, i.e., the "loadings". The eigenvalues of the eigenvectors are proportional to the fraction of variance that is explained by the single axes or components and can be used to assess the importance of single "processes". Usually, only the axes with the highest eigenvalues are interpreted, e.g., components with an eigenvalue exceeding one.

Gaussian distribution of the data is a crucial prerequisite of the principal component analysis when the data set is rather small. In this study, however, the data set comprises some thousand data points where effects of skewed distributions are negligible. Furthermore, the Isomap approach does not require any specific distribution of the data. Thus, for the sake of comparability, the data set was not adjusted to a Gaussian distribution prior to the principal component analysis.

Isometric Feature Mapping (Isomap)

Principal component analysis is equal to the classical multidimensional scaling (CMDS) if Euclidean distances are used (Gámez et al. 2004). The CMDS aims at preserving the interpoint distances of the high-dimensional data set while projecting the data into a low dimensional space. The solution is found by an eigenvalue decomposition of the distance matrix. Usually, only the first eigenvectors (sorted by decreasing eigenvalues) are considered for the subsequent analysis.

The Isometric Feature Mapping (Isomap) method is a variant of the CMDS approach which differs with respect to the determination of the distance matrix (Tenenbaum et al. 2000). In the first step, for every data point the k nearest neighbors are determined. Here, Euclidian distances were used. In the next step, the full distance matrix is set up, where distances are calculated as the smallest sum of the interpoint distances determined in the first step. These geodesic distances correspond to those of a road system where every town is directly linked only to the k nearest towns. These geodesic distances are equal to or larger than the corresponding direct distances used by planes. The approach aims at mapping nonlinear manifolds by using a locally linear approach. The less linear the manifold in the data set, the more likely is the Isomap approach to outperform linear methods which has in fact been shown in some studies (Tenenbaum et al. 2000, Gámez et al. 2004, Mahecha et al. 2007). The impact of k on the Isomap performance was investigated by systematical variation of this parameter. In this study, the best performance was found for k = 2000.

The Isomap analysis gives components that can be interpreted correspondingly to the linear principal components. However, as they are not necessarily linear, it is not sufficient to use the Pearson

correlation coefficient between single components and parameters. Instead, scatter plots were used in this study. In this study, the package "vegan" by Oksanen et al. (2007) has been used for the Isomap analyis.

Measure of Performance

There are different measures of performance for the ordination methods. For the principal component analysis that is based on an eigenvalue decomposition of the covariance matrix the fraction of explained variance is proportional to the eigenvalues. However, that approach cannot be followed for the Isomap approach which is based on an eigenvalue decomposition of the distance matrix of the data. Here a more general approach is used for evaluating the performance of ordination methods. It is based on the Pearson correlation between the interpoint distances in the high-dimensional data space and in the low-dimensional projection. Both measures are related, and both give a value of one for a perfect fit, and close to zero for a very poor fit. However, they do not match exactly and thus cannot directly be compared.

3.2 Low-pass Filtering of Time Series

One focus of this study was on investigating long-term shifts of the effect of different processes. Linear trend analysis was not considered to be an adequate approach for environmental data. Due to substantial short-term variability, the component scores had to be smoothed. A common way to do that is to calculate mean values of distinct or sliding windows of a certain length. Often annual mean values are selected as many environmental data exhibit a pronounced seasonal pattern. This approach was not used here as the sampling dates were not always equally spread over the year. Besides, considering only one mean value per year implies a considerable loss of information compared to weekly or monthly sampled data.

Instead, a low-pass filter was applied to the time series of component scores at single sites. The approach is based on a spectrum analysis. The samples had not always been taken at regular intervals. Thus, a Fourier analysis could not be performed. Instead, the approach by Lomb-Scargle was used. The approach and the package "LombScargle" that was used for this study is described by Glynn et al. (2006). The package is available at http://research.stowers-institute.org/efg/2005/LombScargle/R/index.htm. Based on the results of the spectrum analysis, the low-pass filtering was performed by reconstructing the data using period lengths larger than a year only.

4. Results

4.1 Explained Variance

Fig. 2 gives the Pearson correlation between the interpoint distances in the 13-dimensional data space and in the low-dimensional projection. The components are ordered according to the fraction of variance they explain. About 94% of the variance is represented by the first four Isomap components. These components are slightly more effective with respect to representing the variance of the data compared to the linear principal component approach, whereas there are only minor differences for the fifth and sixth component. In the following, only the first four components will be considered.

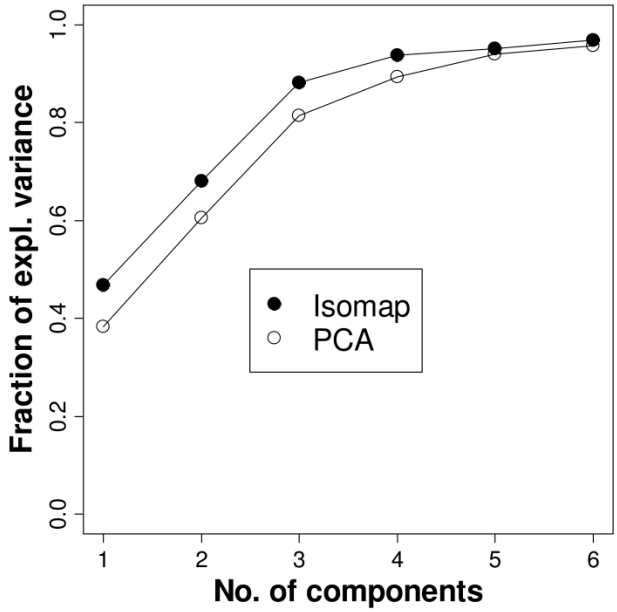

Fig. 2: Variance explained by the first six principal components and Isomap components.

4.2 Identification of Processes

The next step aims at ascribing these components to biogeochemical processes. To that end, the relationships between single solutes and component scores are investigated as well as spatial and temporal patterns.

1. Component: Redox Status

The first component represents 46.8% of the variance of the data set. The component is positively correlated with NO_3^-, SO_4^{2-}, Al, Ca, K and Mg, and negatively correlated with Fe and DOC concentration (Fig. 3). Appreciable NO_3^- concentrations are restricted to component scores > -2, whereas the opposite is true for Fe. The relationship between SO_4^{2-} and the first component can be split into two distinct groups with slightly different slopes and offsets. The point of intersection of

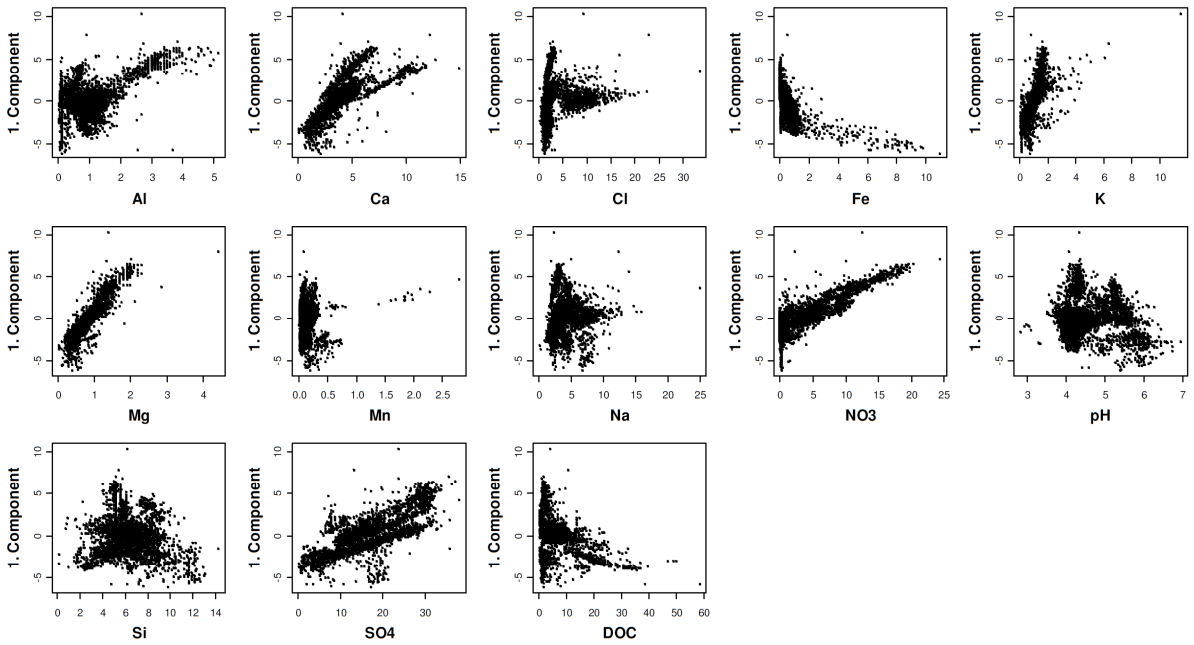

Fig. 3: Loadings of the first Isomap component. Concentrations are given in [mg/l].

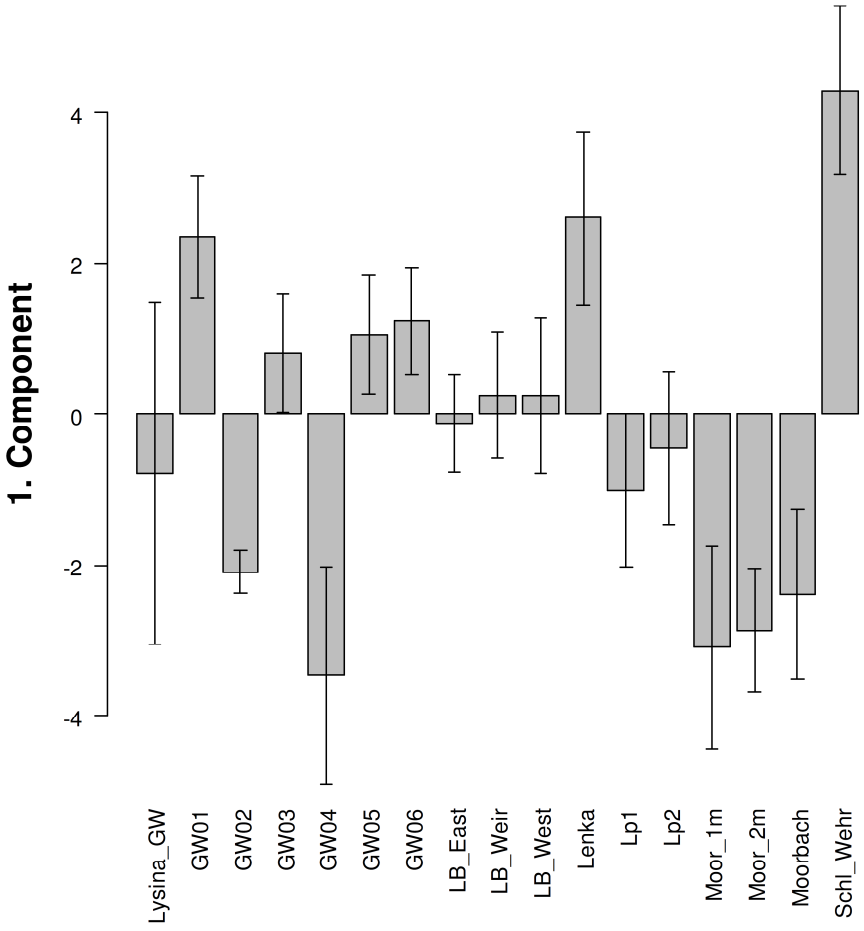

Fig. 4: Mean values and standard deviation of the first component scores for the different sampling sites.

both groups with the y-axis is roughly between -3 and -4, that is, slightly less compared to that of the NO_3^- data. A similar pattern emerges for Ca, which is presumably due to the same reasons. However, for the sake of brevity this is not presented in more detail.

The relationship between NO_3^-, SO_4^{2-}, Fe concentration and the first component resembles the well-known redox sequence: The lower the redox potential, the more pronounced is denitrification, desulfurication and Fe reduction. The redox potential in the two catchments presumably is the lowest in the wetland soils, which exhibit the highest DOC concentration. In addition, NO_3^- and SO_4^{2-} are the prevailing anions in groundwater and streamwater. As the end products of denitrification and desulfurication are mostly released via degassing and precipitation, these processes result in a decrease of ionic strength which is reflected by a corresponding decrease of the concentration of most of the cations.

The lowest component scores, i.e., the most reduced water was found in the riparian wetlands of the Lehstenbach catchment, that is, for the deep groundwater wells GW02 and GW04, for shallow groundwater wells Moor_1m and Moor_2m and in the Moorbach stream that drains a wetland area close to the catchment outlet (Fig. 4, cf. Fig. 1). Please note that the redox component is not a measure of the redox potential of the water sample. In all streams including the Moorbach stream oxygen saturation usually was fairly high. In contrast, the redox component seems to be a measure of to what degree redox processes had an impact on water quality before it reached the stream. Consequently, this component can be interpreted corresponding to a shift of nitrate-^{15}N or sulfate-^{34}S values.

The upslope springs in both catchments (Lenka and Schl_Wehr), and the upslope groundwater well GW01 exhibit the highest values. It is interesting to note that the mean redox component score of the Lehstenbach catchment runoff (LB_Weir) is higher than those of the Lysina Lp2 stream, and that of Lysina stream Lp1 is even lower, which corresponds roughly to the fraction of riparian wetlands in the respective catchments.

2. Component: Topsoil

The second component adds another 21.3% of explained variance to that of the first component. High scores of this component are associated with high Al and DOC concentrations, low Si and Na concentration and low pH values (Fig. 5). This is typical for the soil solution in the uppermost horizons in both catchments. High Al concentrations and low pH are due to long-term deposition of sulfate and other acidifying solutes that leached base cations from the topsoil. However, due to the strong decline of acidifying deposition during the last two decades, there is no clear relationship between this topsoil component and SO_4^{2-} concentration. Sulfate concentration is now the highest in groundwater of medium depth (Büttcher 2001, Lischeid et al. 2003, Lischeid et al. 2004). There is a strong but non-linear relationship between this component and the pH values. Silica and Na originate

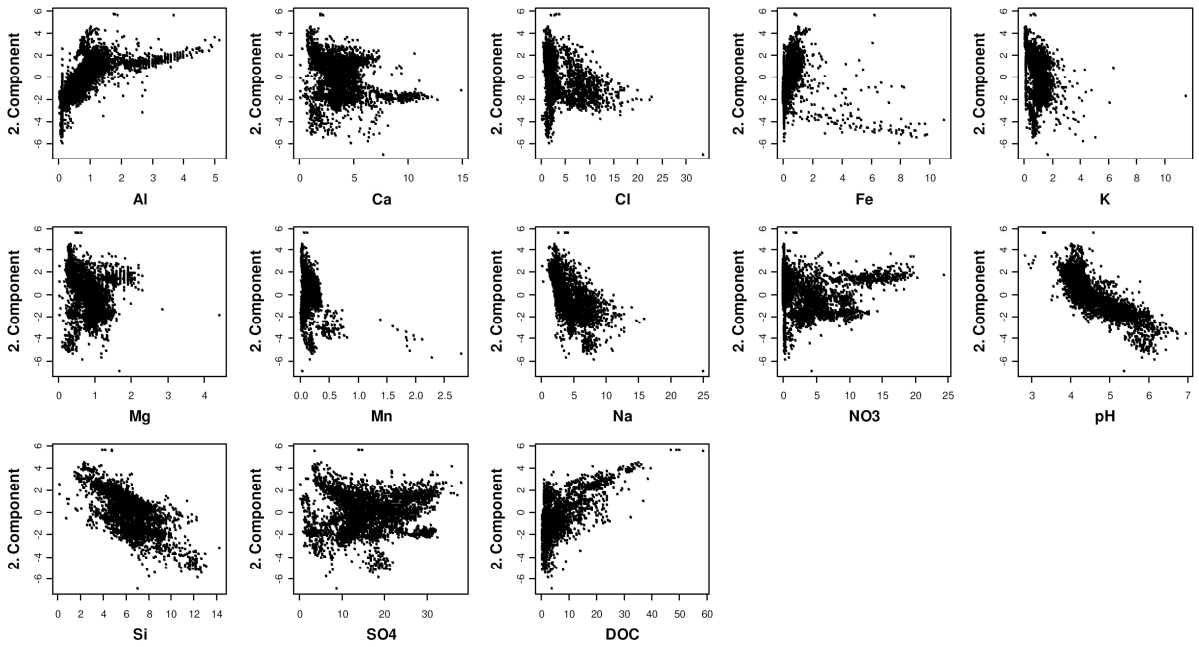

Fig. 5: Loadings of the second Isomap component. Concentrations are given in [mg/l].

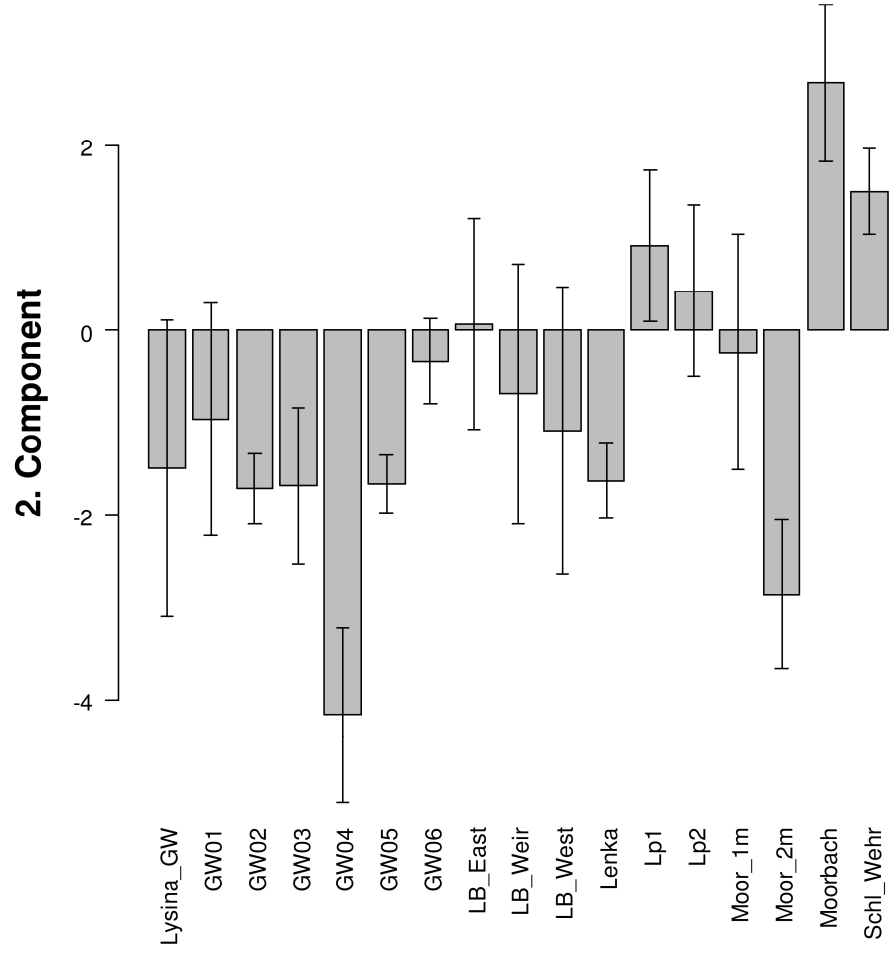

Fig. 6: Mean values and standard deviation of the second component scores for the different sampling sites.

mainly from weathering of feldspars of the granite bedrock (Weyer et al. 2008). Mobilization of Si has been shown to exhibit very slow kinetics in the Lehstenbach catchment, allowing to use Si concentration as a proxy for groundwater residence time (Lischeid et al. 2002).

Most of the scatter of the relationship between Fe concentration and the topsoil component can be ascribed to the redox component, especially for the high Fe concentration data. Putting aside this fraction of the data, there is an increase of Fe concentration with increasing component scores which corresponds to Fe(III) mobilization by low pH values around 4.

The highest topsoil component scores were observed in the Lehstenbach streams Moorbach and Schl_Wehr that drain rather small subcatchments (Fig. 5). The lowest scores were found in the Lehstenbach groundwater wells GW04 and the Moor_2m wells. According to the results of a groundwater model, well GW04 samples groundwater with the longest residence time in the Lehstenbach catchment (Lischeid et al. 2003). The Moor_2m shallow groundwater wells are screened in a layer of very low hydraulic conductivity at 2 m depth which would correspond to a long residence time in spite of shallow depth. Comparing the three catchment outlet streams LB_Weir (Lehstenbach), Lp2 (Lysina) and Lp1 (Lysina), the topsoil component scores increase with the fraction of riparian wetlands in the respective catchments.

In the streams the topsoil component is closely related to discharge, although with different shapes (Fig. 7). Thus, this component could be used for chemical hydrograph separation similarly to the approaches used by Buzek et al. (1995) and Lischeid et al. (2002).

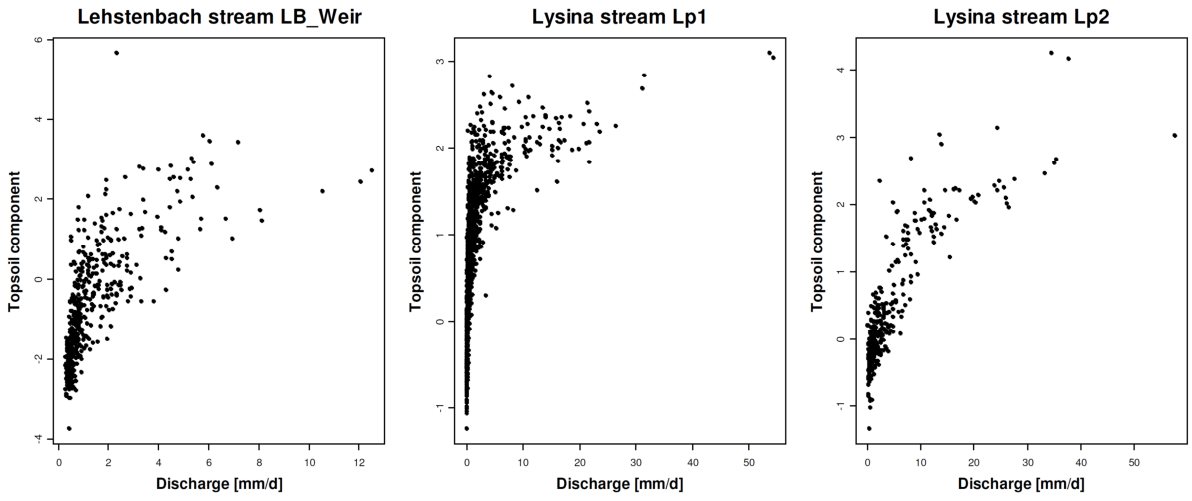

Fig. 7: Topsoil component scores versus discharge at the catchment outlets.

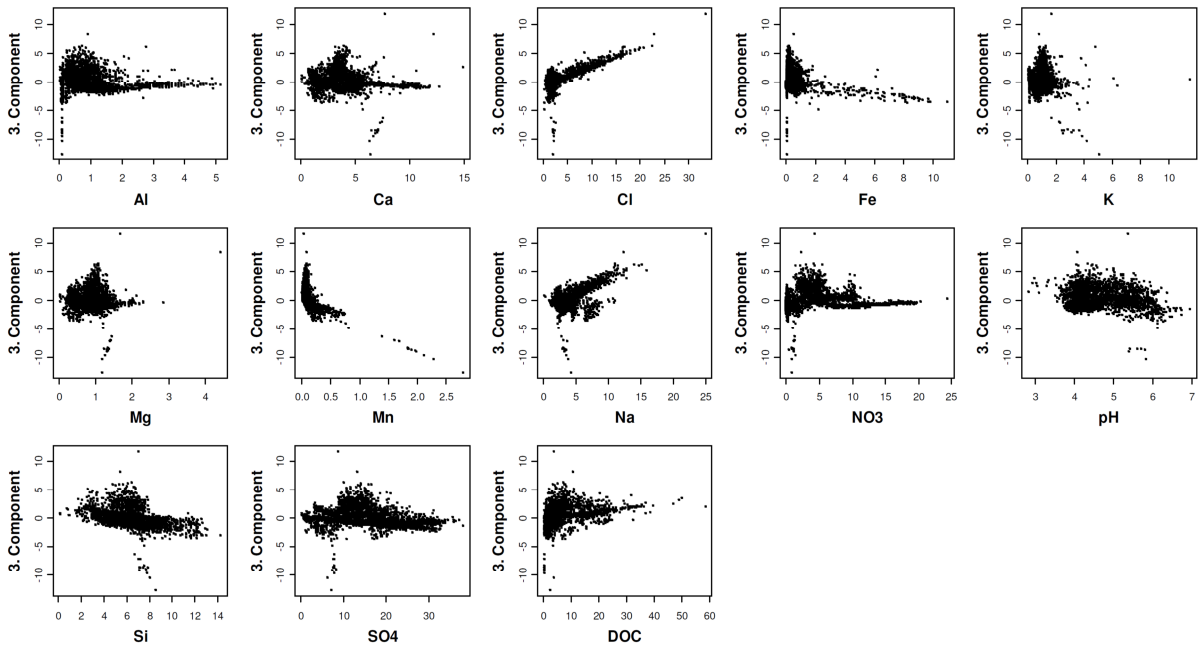

Fig. 8: Loadings of the third Isomap component. Concentrations are given in [mg/l].

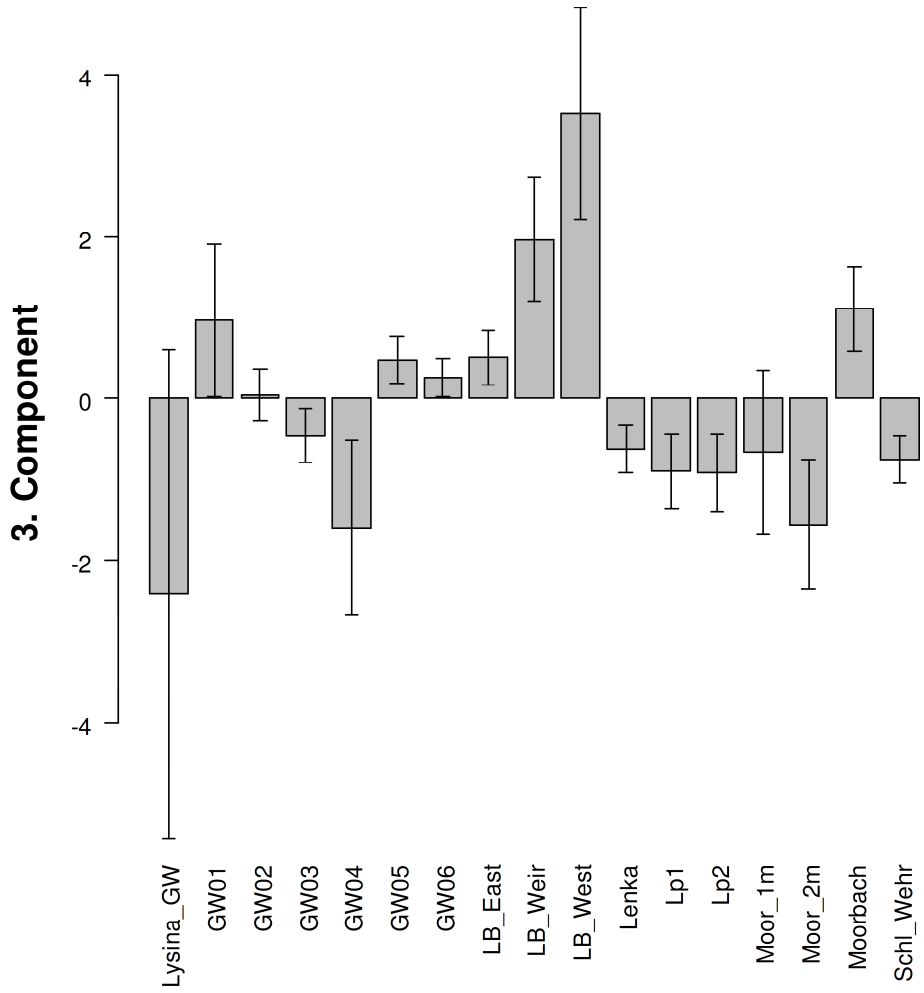

Fig. 9: Mean values and standard deviation of the third component scores for the different sampling sites.

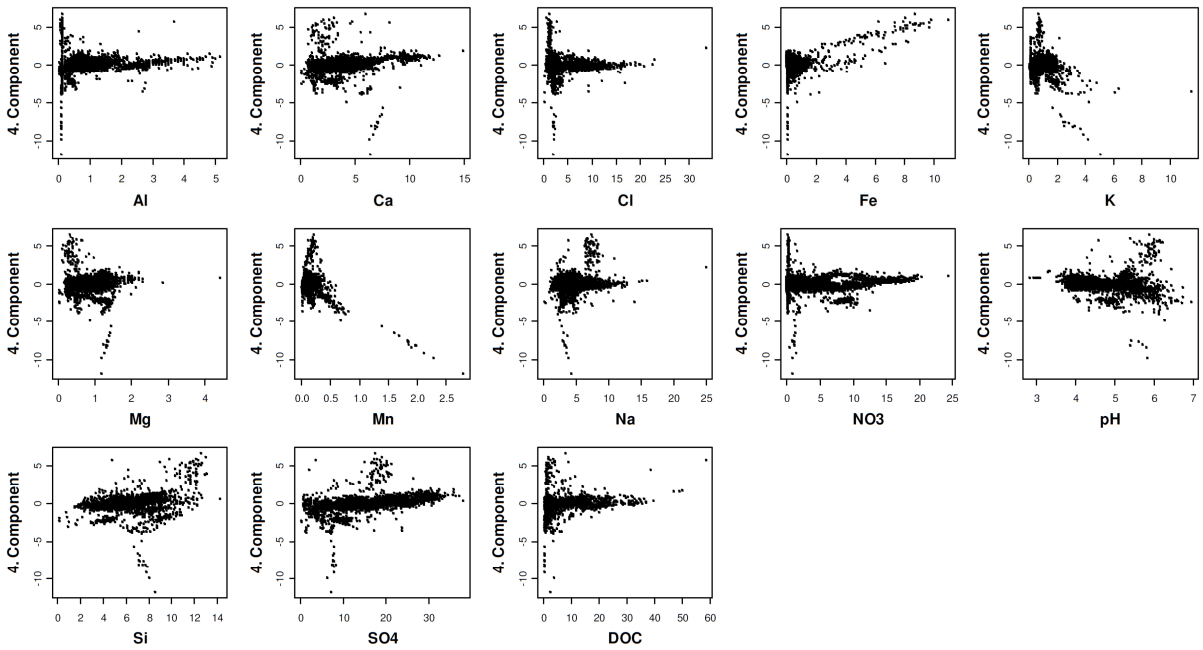

Fig. 10: Loadings of the fourth Isomap component. Concentrations are given in [mg/l].

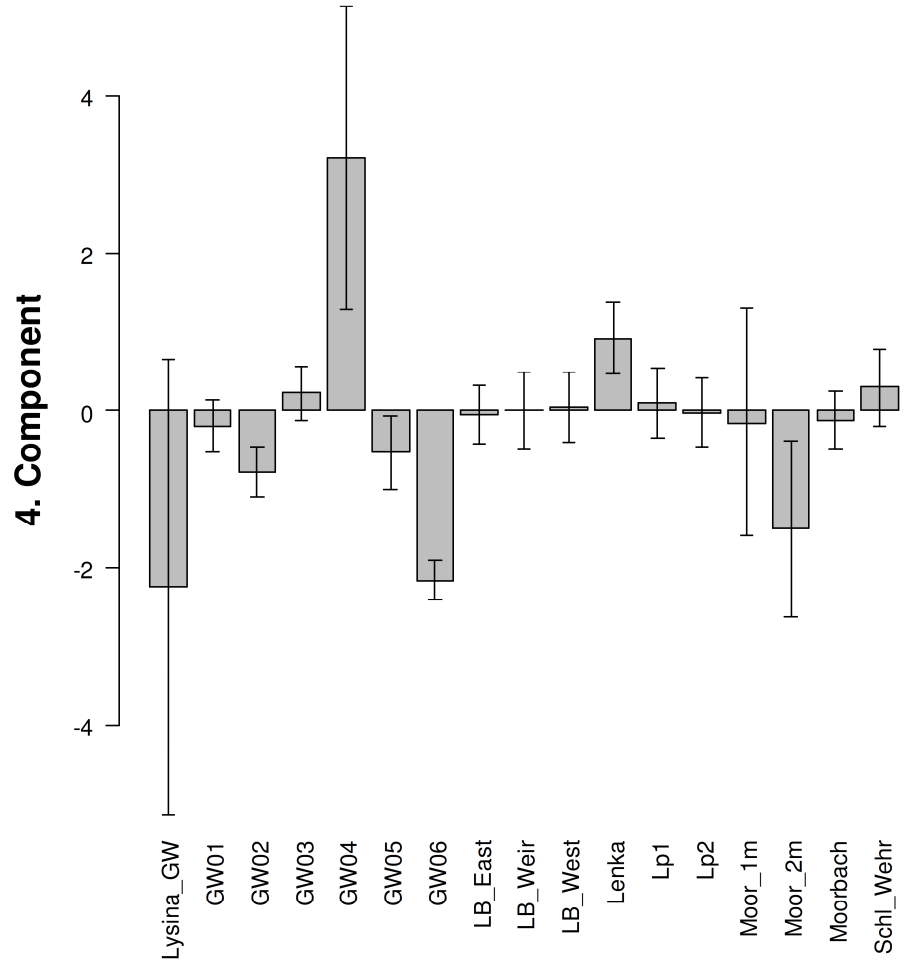

Fig. 11: Mean values and standard deviation of the fourth component scores for the different sampling sites.

3. Component: Road Salt

The third component is correlated with Cl^- and Na concentration, and inversely related to Mn concentration (Fig. 8). This component explains another 20.1 % of the variance of the data. The highest scores were observed in the Lehstenbach groundwater well GW01, in the Lehstenbach runoff LB_Weir and especially in its tributary LB_West (Fig. 9). These sites are affected by road salt application of a public road in the western part of the catchment (cf. Fig. 1). Because this effect is restricted to some sites only, it will not be considered in the following.

4. Component: Sulfate Contamination

The fourth component adds another 5.5% of explained variance to that given by the first three components. Correspondingly, the relationships between single solutes and the component scores are more difficult to interpret because they are masked by the effects of the first three components. Focusing on the bulk of the data, sulfate, Al and Ca concentration seem to increase, and pH to decrease with increasing component scores (Fig. 10). Taking into account that most of the variance of these solutes is explained by the first three components, it is concluded that this component is associated with effects of sulfate contamination in addition to those described by the redox component.

A clear increase of Mn concentration with decreasing component scores is restricted to the lower quantile of component scores (Fig. 10). Component scores less than -5 are restricted to the deepest groundwater well of the Lysina catchment which is gauged between 4.2 and 4.4 m below surface. At this well K and Si concentration shows a similar relationship with that component, whereas the inverse pattern emerges for Ca and Mg (Fig. 10). This could point to a displacement of geogenic compounds by Ca and Mg that were associated with high sulfate deposition rates in the last decades. The samples with the highest scores of that component (exceeding +2) were taken at well GW04 and in the wetland piezometers Moor_1m at 1 m depth in the Lehstenbach catchment (Fig. 11). At GW04, oxygen concentration was almost, and at Moor_1m often close to zero. Only for these samples there was a positive correlation between component scores and Fe concentrations (Fig. 10).

Besides, the upslope springs Lenka (Lysina) and Schl_Wehr (Lehstenbach) show rather high values. These sites sample a high fraction of intermediate depth groundwater that now exhibits the highest SO_4^{2-} contamination (Büttcher 2000, Lischeid et al. 2003).

4.3 Time series

One focus of this study was to investigate if there are some common trends of single processes, including non-linear long-term patterns. To that end a low-pass filter was applied to the component scores. Please note that the low-pass filtered part of the fraction represents different fractions of the variance of the respective time series, due to different short-term variations at different sites. Besides,

the beginning and end of the time series have to be interpreted with care, when only few samples were available from these periods. This holds especially true for the last years at the Lehstenbach catchment runoff (LB_Weir) and upslope spring (Schl_Wehr). Thus, the supporting points are given as black points in the graphs of components (Fig. 12-15).

Meteorological Data

The meteorological data were low-pass filtered in the same way as the water quality data. Fig. 12 shows the long-term trends 1989-2007, normalized to the respective mean values in order to facilitate comparison between the two parameters. Please note that start and end of the single curves have to be interpreted with caution.

Both at Lysina and Braunersgrün, precipitation was fairly low during the early 1990s. At Lehstenbach and Braunersgrün precipitation exhibited a minor peak at 2001 and a minor decrease thereafter. The variance of the low-pass filtered temperature data was smaller compared to precipitation. Minor peaks were observed around 1993 and 2001, minor lows in 1997 and 2004.

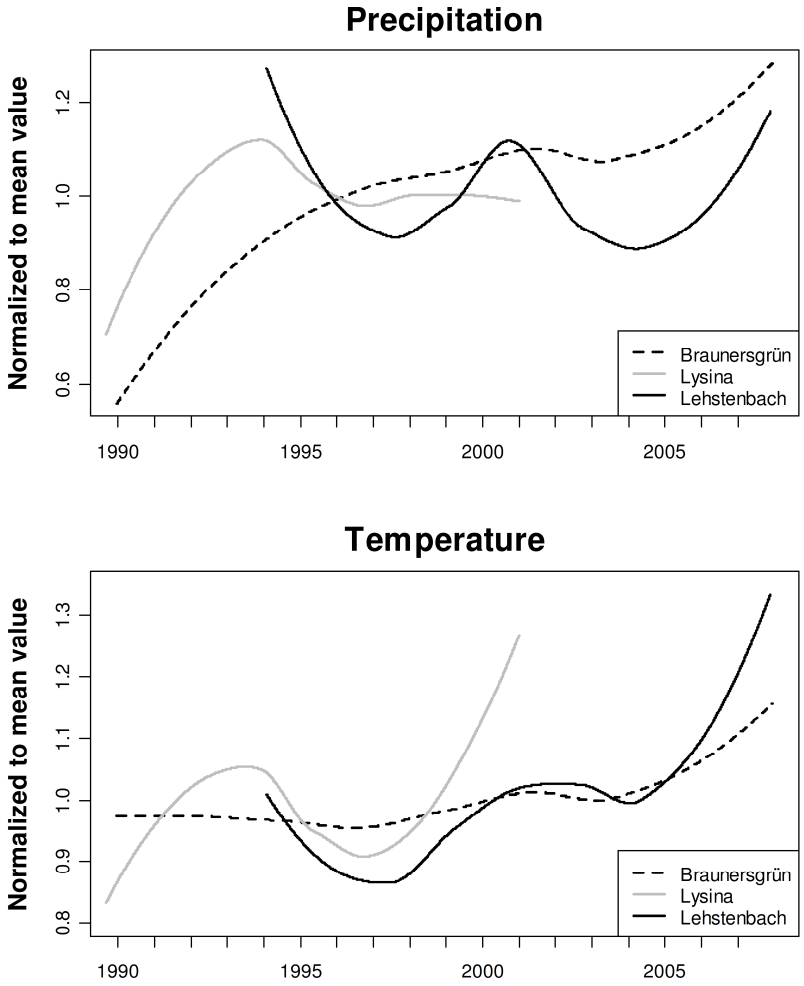

Fig. 12: Low-pass filtered time series of precipitation and air temperature at Braunersgrün, Lysina and Lehstenbach 1989-2007, normalized to mean values for the whole period.

Redox Component

Both of the Lysina streams (Lp1, Lp2), the Lysina upslope spring (Lenka), as well as the Lehstenbach catchment runoff (LB_Weir) and upslope spring (Schl_Wehr) and one of the deep groundwater wells (GW03) exhibited a decrease during the last two decades (Fig. 13). However, these three Lehstenbach sites show a transient increase or a change of slope in the 1990s. In contrast, the redox component scores at the Lehstenbach groundwater wells GW01, GW04, and GW05 and GW06 peak between 1995 and 2003. Around 1995 there is an intermediate or minor peak at many sites in the Lehstenbach catchment. In contrast, at the Lehstenbach well GW02 there is hardly any clear long-term shift of the redox component.

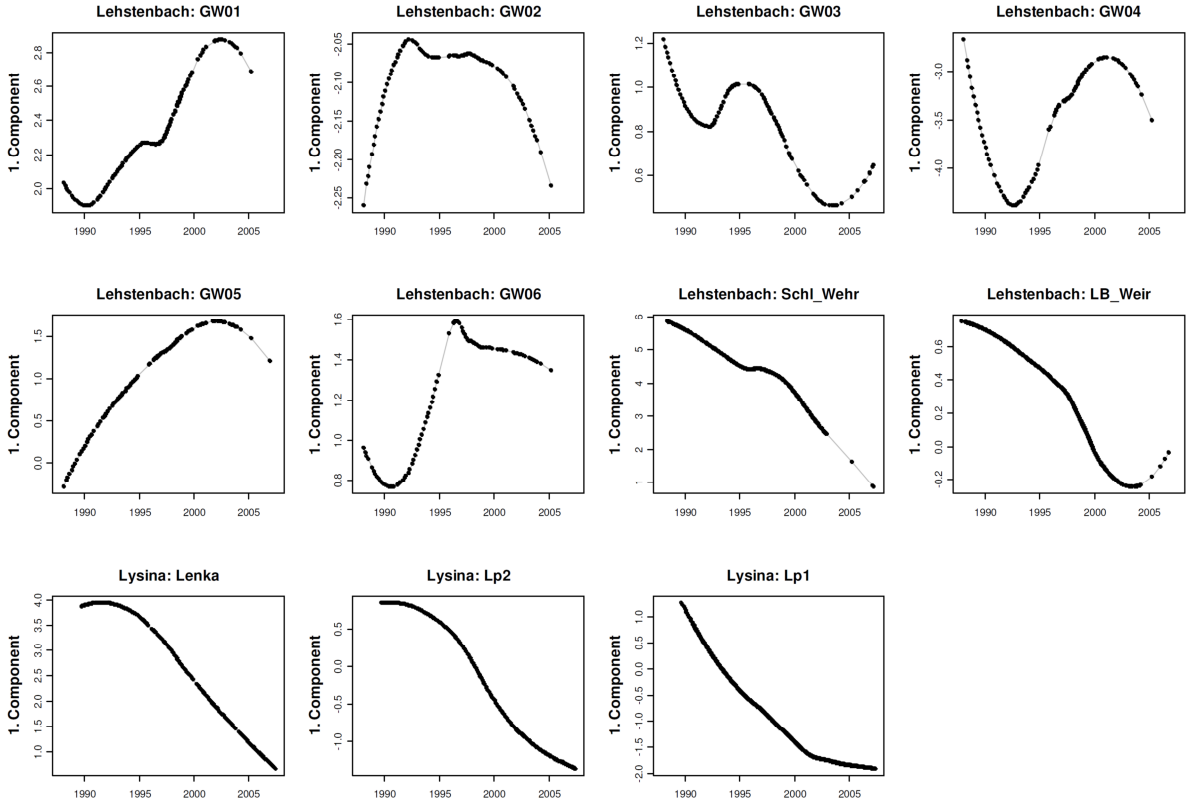

Fig. 13: Low-pass filtered time series of the first component at selected sampling sites.

Topsoil Component

The low-pass filtered time series show two different patterns: Either there is a minimum in the late 1990s, and a steep increase thereafter (Lysina streams Lp1, Lp2, Lysina upslope spring Lenka), or a pronounced decrease during the first years, a peak 1995-2000, and decrease again thereafter (Lehstenbach groundwater wells). The latter behavior reflects that of low-pass temperature data, although inversely and slightly lagging behind temperature (cf. Fig. 12). The Lehstenbach stream (LB_Weir) and upslope spring (Schl_Wehr) exhibit features of both groups (Fig. 14). Only at well

GW01 the long-term behavior of the topsoil component seems to parallel that of precipitation between 1995 and 2003. It has been known prior to this study that groundwater quality at this well often reflects preferential flow from the topsoil (Lischeid and Bittersohl 2008).

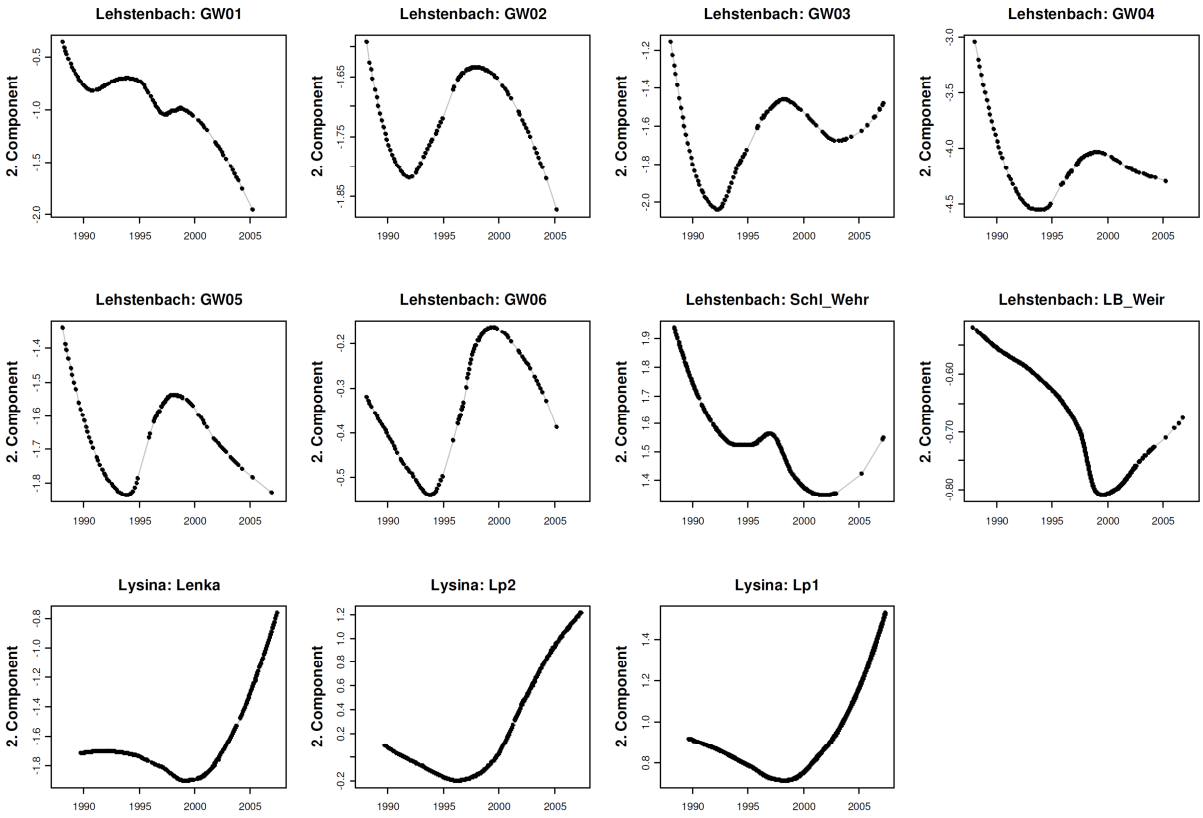

Fig. 14: Low-pass filtered time series of the second component at selected sampling sites.

Sulfate Contamination Component

A clear decrease of the SO_4^{2-} contamination component was observed at the Lysina streams (LP1, LP2) and the Lehstenbach upslope spring (Schl_Wehr). At the Lehstenbach well GW01 and the Lysina upslope spring Lenka this component peaked in 1995-1997 and clearly decreased thereafter. In contrast, most of the Lehstenbach groundwater wells and the Lehstenbach catchment runoff (LB_Weir) exhibit two peaks, the first one between 1990-1995 and the second one between 2003 and 2007 (Fig. 15). This behavior, especially at GW03, resembles that of low-pass filtered temperature in the same catchment (cf. Fig. 12).

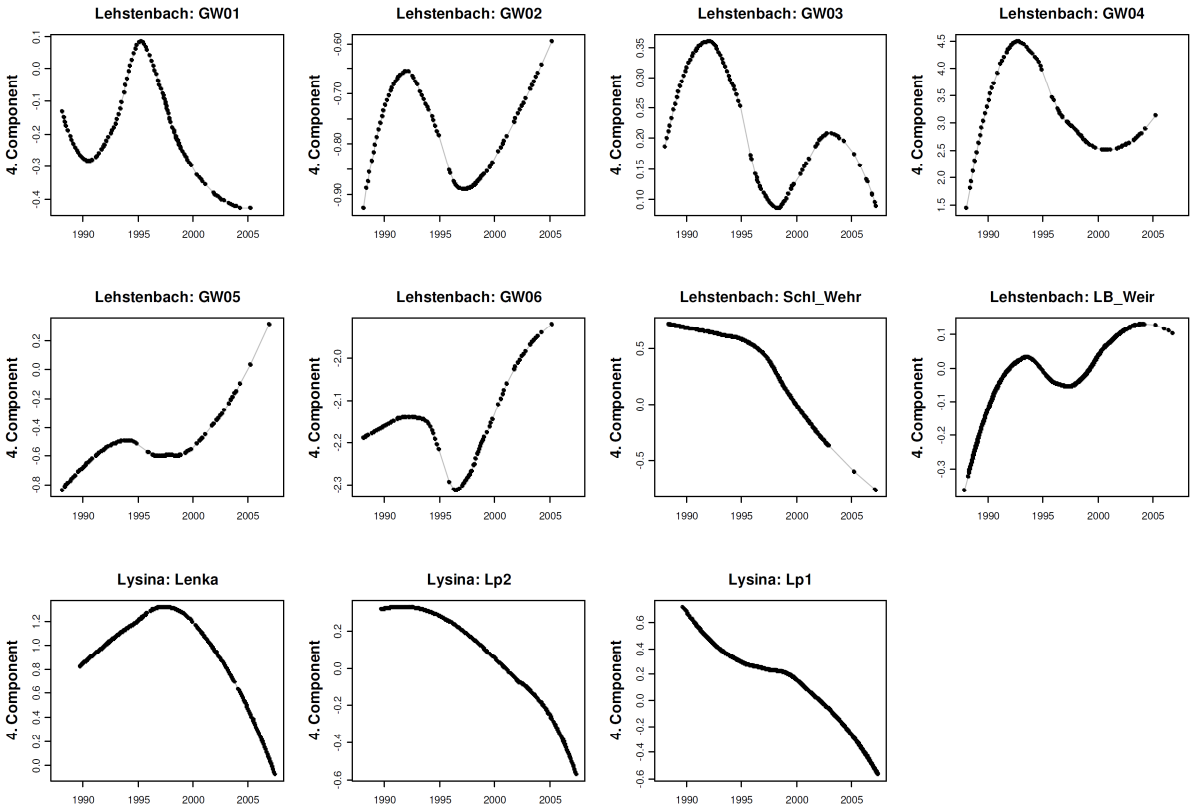

Fig. 15: Low-pass filtered time series of the fourth component at selected sampling sites.

4.4 Interplay of Different Processes

It has been stated prior to the study that single solutes were affected by different processes. This has been investigated in more detail using time series of the Lysina upslope spring Lenka and the Lehstenbach groundwater well GW01. To that end the prevailing anions NO_3^- and SO_4^{2-} have been selected.

Lysina upslope spring Lenka

The Lenka spring was unique among all sampling sites in the Lysina and Lehstenbach catchment as it exhibited a highly significant and nearly perfect linear decrease of NO_3^- concentration (Fig. 16). In contrast, SO_4^{2-} concentration slightly increased until 1995 and clearly decreased thereafter (Fig. 16). The redox component roughly paralled the SO_4^{2-} time series and clearly decreased after 1994. In contrast, the SO_4^{2-} contamination component increased until 1998 and decreased thereafter. The topsoil component remained fairly stable until 2001 and started increasing during the last years of the study.

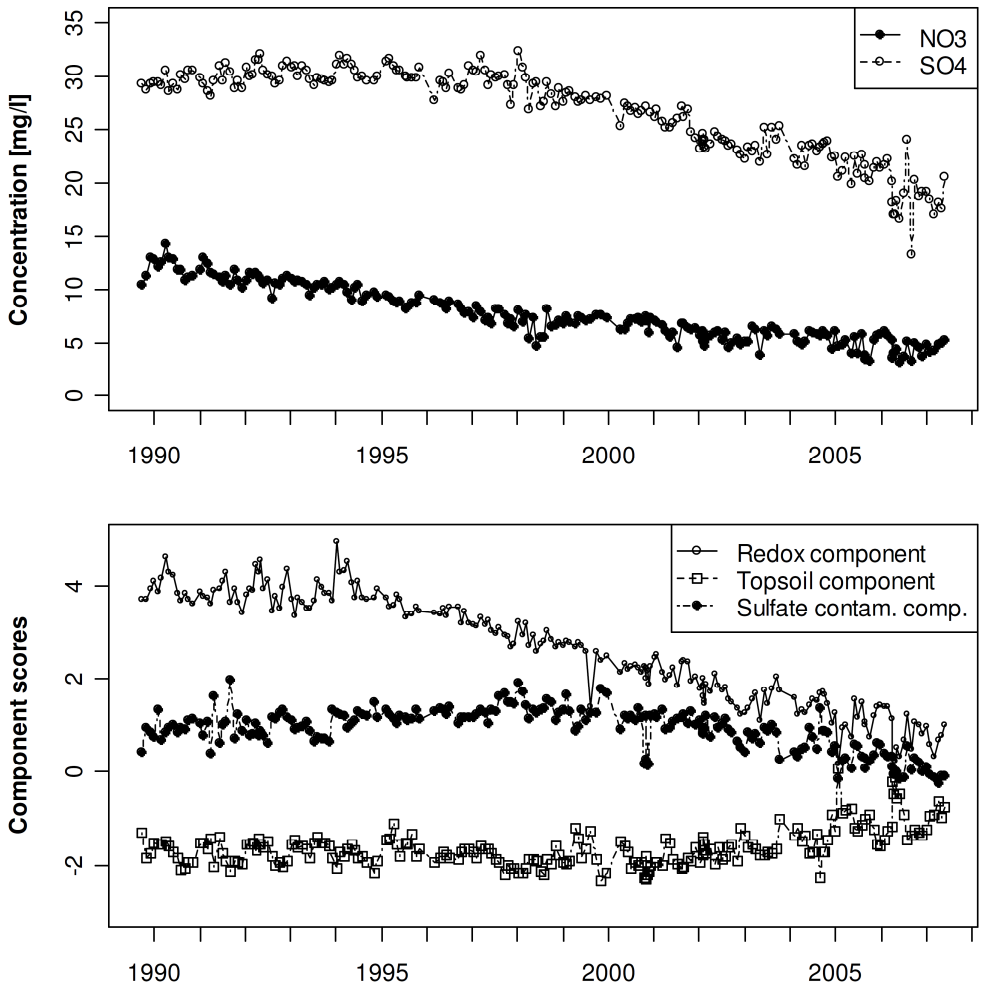

Fig. 16: Time series of NO_3 and SO_4 concentration (upper panel) and component scores (lower panel) at the Lysina upslope spring Lenka.

Sulfate deposition in this region decreased tremendously since the end of 1970s. Due to the effect of SO_4^{2-} sorption to the matrix, the SUNFLOW sulfate model predicted an increase of SO_4^{2-} contamination at this site until the 1990s (Büttcher 2001) which is confirmed by the SO_4^{2-} contamination component. In addition, part of the SO_4^{2-} decrease seems to be due to increasingly less oxic conditions, as suggested by the decrease of the redox component after 1994 (Fig. 16). However, NO_3^- concentration started to decrease a few years before, coinciding with an initial increase of SO_4^{2-} concentration. This could point to an antagonism between the two anions.

Last, but not least the topsoil component did not start to increase before 2001/2002. In August 2002 the Lysina catchment was affected by the severe rainstorm that caused the Elbe flood further downstream, whereas there was no exceptional rainfall in the Lehstenbach catchment. It is likely that the increasing topsoil component amplified the decrease of SO_4^{2-} concentration in the spring water because the topsoil layers showed much more pronounced recovery of SO_4^{2-} deposition (Büttcher 2001, Shanley et al. 2004).

Lehstenbach groundwater well GW01

In contrast to the Lenka spring water, groundwater at the Lehstenbach well GW01 exhibits substantially higher short-term variability, especially for SO_4^{2-} concentration (Fig. 17). Sulfate concentration often increased by a factor of two during rainy or snowmelt periods in the dormant season. In fact, SO_4^{2-} concentration is closely related to groundwater level at this site (not shown). The SO_4^{2-} concentration peaks coincide with substantial increases of the topsoil component (Fig. 17), indicating preferential flow phenomena. This is especially true for fall and winter 1998, a period of extensive rainfall (Lischeid et al. 2002). In addition, the redox component exhibits synchronous peaks, indicating preferential infiltration of oxic water from the topsoil. However, only a few of these peaks are reflected by a corresponding increase of NO_3^- concentration (Fig. 17). In the long-term, the redox component showed an almost linear increase 1990-2004, whereas the SO_4^{2-} contamination component peaked around 1997 and decreased thereafter. Nitrate in the groundwater slightly decreased until 1995 in spite of the decreasing redox component, but parallel to the increasing SO_4^{2-} contamination component. Like at Lysina, this could indicate an antagonism between NO_3^- and SO_4^{2-}. After 1995, the redox component increased and the SO_4^{2-} contamination component decreased at this well which seemed to have compensated each other, resulting in constant SO_4^{2-} and NO_3^- concentration.

Antagonism between NO_3^- and SO_4^{2-}

Both at Lenka and GW01 the data seem to indicate an antagonism between NO_3^- and SO_4^{2-} concentration. Thus, the relationship between the redox component, the SO_4^{2-} contamination component and NO_3^- concentration was investigated. This was rendered difficult due to some substantial outliers. Ignoring component scores less than the 0.05 and exceeding the 0.95 quantile, however, reveals a clear relationship (Fig. 18): Nitrate concentration does not only increase with increasing redox component scores, but decreases with increasing SO_4^{2-} contamination component scores also. Thus, e.g., the transition between white plots indicating very low NO_3^- concentration and slightly grey symbols, indicating higher NO_3^- concentration, occurs along a line that is inclined toward both axes. In fact, 74% of the variance of NO_3^- concentration in this data set can be explained by linear regression with the redox and the SO_4^{2-} contamination component, where the latter exhibits a negative regression coefficient (Tab. 2).

Tab. 2: Coefficients of multivariate linear regression of NO_3^- concentration as a linear function of redox component and SO_4^{2-} contamination component scores, ignoring component scores less than the 0.05 and larger than the 0.95 quantile.

	Coefficient of regression	**Level of significance**
Redox component	+0.421	$< 2 \cdot 10^{-16}$
SO_4^{2-} contamination component	-0.359	$< 2 \cdot 10^{-16}$

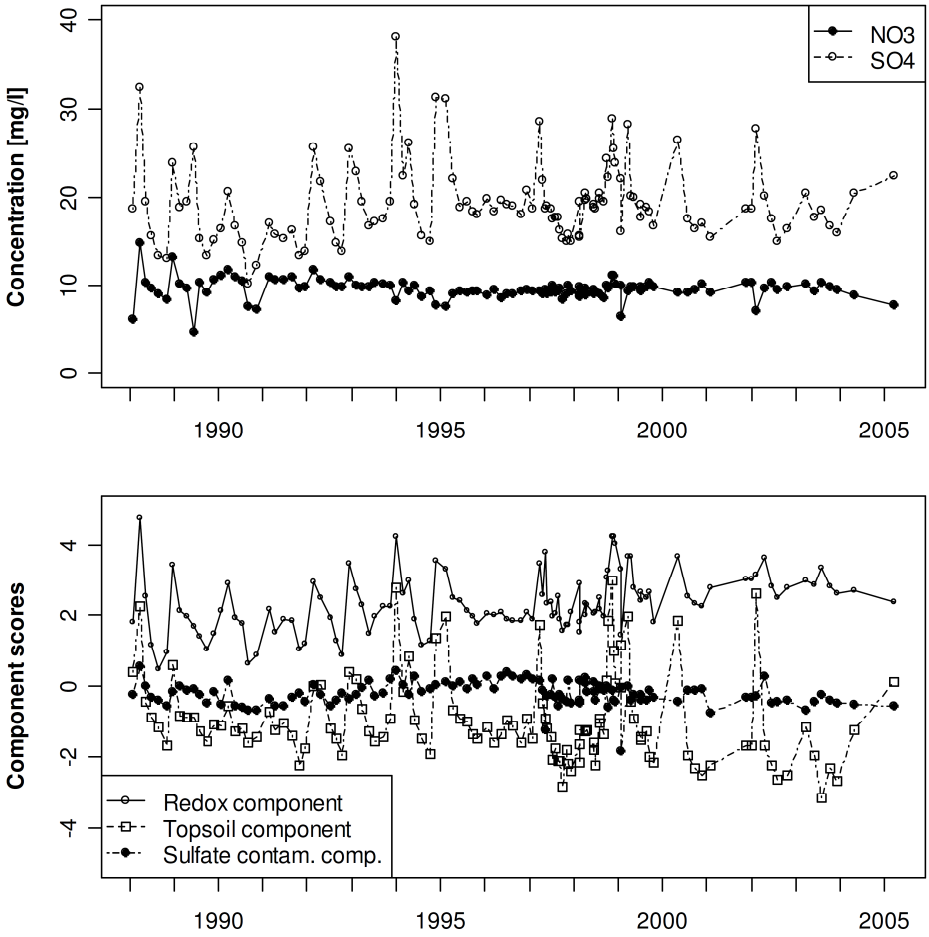

Fig. 17: Time series of NO_3 and SO_4 concentration (upper panel) and component scores (lower panel) at the Lehstenbach well GW01.

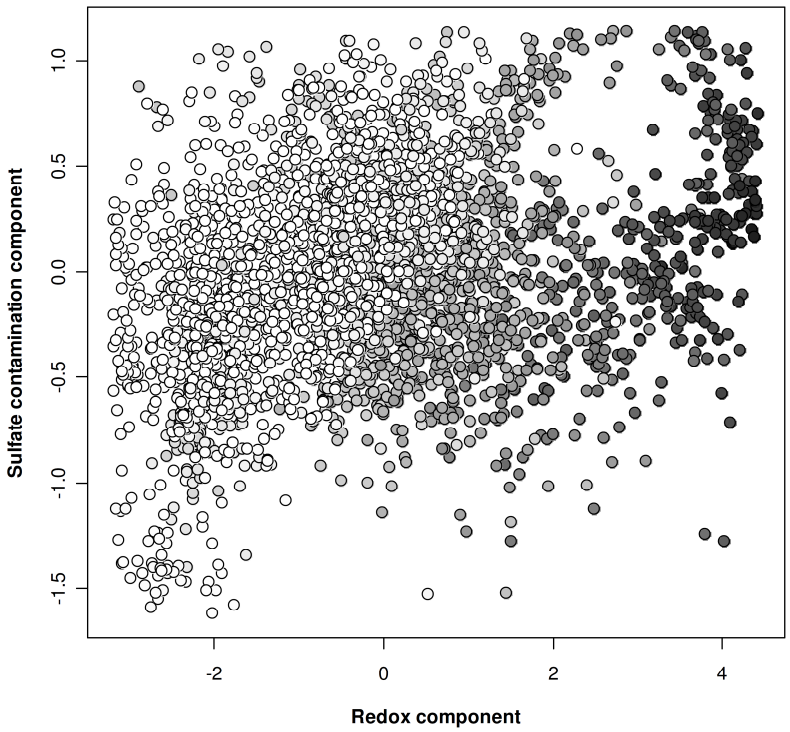

Fig. 18: Nitrate concentration (white: minimum, black: maximum) depending on scores of the first and fourth component. For the sake of clarity extreme values of the components are not shown.

5. Discussion

5.1 Ad methods

The objective of the study was to identify the key processes that affect groundwater and surface water quality in a region of the East Bavarian-West Bohemian crystalline basement and to investigate long-term trends of these processes. To that, non-linear statistical methods were used to account for the pronounced non-linearity of environmental data.

The non-linear Isometric Feature Mapping proved to be slightly superior to the linear principal component analysis in terms of explained variance of the first components (Fig. 2). The difference is smaller compared to some other studies (Tenenbaum et al. 2000, Mahecha et al. 2007). Correspondingly, the first components of the linear and of the non-linear principal component analysis were highly correlated. The larger the optimal k parameter for setting up the geodesic distance matrix for the Isomap analysis, the less the Isomap results differ from that of the linear principal component analysis. In this study, the optimal k was approximately equal to half the number of samples, pointing to rather weak non-linearities. However, the Isomap components were easier to interpret and to assign to biogeochemical processes. The same has been found by Lischeid and Bittersohl (2008).

Time series of environmental parameters usually exhibit substantial short-term variability, which is often traced back to a complex interplay of different processes. Water resources management, however, needs to consider long-term shifts. These do not necessarily show up as linear trends, and in fact rarely do so for longer periods. Thus, a low-pass filter was applied that was able to extract a rather smooth long-term pattern from the time series. As many hydrochemical time series exhibit pronounced seasonality, the cut-off for the considered periods was set equal to one year length.

Similarly to, e.g., linear regression, the fit of a low-pass filter to the data has to be considered with care for the beginning and for the end of the time series. The chosen approach is based on a spectrum analysis. Thus, it tends to fit low-frequent oscillations to the data. In this study, these structures have not been considered when they were restricted to the first or final two years of the time series.

5.2 Ad results

Determination of the principal components does not require any a priori assumptions. In contrast, assigning components to biogeochemical processes is subject to expert's choice and can be questioned. It is primarily based on the relationships between component scores and measured parameters, but considering spatial and temporal patterns of the component scores as well.

Redox and Sulfate Contamination Components

The first component, which explained nearly half of the variance of the data was interpreted as a redox component. This component provides a measure of the impact of redox processes on water quality on its way to the sampling site, but is not a measure of the actual redox potential at the time of sampling. The redox component was not clearly related to oxygen concentration, especially in the streams. For example, the wetland streams Moorbach and Lp1 exhibited low redox component scores in spite of oxygen saturation due to turbulent flow in the streams.

In a preceding study a systematic decrease of the redox component scores with residence time was found in the Lehstenbach deep groundwater, even at the upslope wells outside the wetland areas (Lischeid and Bittersohl 2008). This decrease was associated with a corresponding decrease of NO_3^- concentration, pointing to denitrification. In spite of that, oxygen concentration usually exceeded 6 mg/l in the wells GW01, GW03, GW05 and GW06. In contrast, groundwater oxygen concentration at well GW02 usually was fairly low, and close to zero at well GW04. Legout et al. (2007) could even show that denitrification in the vadose zone of a granite catchment in Brittany played a major role for the nitrogen dynamics. It was assumed that most of the denitrification occured in anoxic micro sites.

On the one hand, NO_3^- and SO_4^{2-} concentration in anoxic groundwater decrease due to denitrification and desulfurication. On the other hand, enhanced input of NO_3^- and SO_4^{2-} due to atmospheric pollution increased the electron acceptor capacity in these micro sites, thus increasing the redox potential of deep soil and groundwater. This effect plays a major role in oxygen-depleted lake sediments but is rarely considered in the vadose zone. The results of this and other studies, however, seem to indicate that the role of anoxic micro sites has been substantially underestimated so far.

Deposition of inorganic nitrogen compounds (mainly dissolved NO_3^- and NH_4) showed substantially less pronounced trends compared to SO_4^{2-}. In deeper soil layers and in the groundwater, only NO_3^- was found in measurable quantities due to oxidation of NH_4 and NH_4 sorption to the soil matrix. During the last two decades nitrogen deposition exceeded the annual uptake by plants and microbes by far in botch catchments. In addition, NO_3^- sorption to the soil matrix is negligible. Thus, spatial and temporal patterns of NO_3^- in the streams and in the deep groundwater were primarily determined by denitrification, resulting in a rather close relationship to the redox component. In contrast, SO_4^{2-} deposition exhibited a tremendous decrease in both catchments and was subject to sorption to the regolith matrix. Consequently, SO_4^{2-} concentration in groundwater and streamwater was related to the flowpath length distribution in the respective subcatchments (Büttcher 2001). This is reflected by the SO_4^{2-} contamination component that explained much of the scatter after subtracting the effect of the redox component (Fig. 3, Fig. 10).

In addition, NO_3^- is slightly negatively correlated with the SO_4^{2-} contamination component. Please note that the relationship of the redox component with NO_3^- is much more pronounced, masking the NO_3^--SO_4^{2-} antagonism. There is some anecdotal evidence in the literature about such an antagonism, e.g.,

by Nakagawa and Iwatsubo (2000). Nodvin et al. (1988) observed a decrease of streamwater SO_4^{2-} concentration after clear cut, which they trace back to increasing SO_4^{2-} sorption due to decreased pH as a consequence of enhanced NO_3^- release. Kaiser and Kaupenjohann (1998) found a corresponding relationship between pH and SO_4^{2-} sorption at two sites close to the Lehstenbach catchment.

Topsoil Component

The topsoil component was identified based on its relationship with Al, DOC, Si and pH (Fig. 5). High Al and DOC concentration, low Si concentration and low pH were usually found in the soil solution of the uppermost horizons (Navrátil et al. 2007, Krám and Hruška unpublished data 2007, Lischeid et al. 2007) that were not included in this analysis. In this data set the highest topsoil component scores were found in the streamwater samples that drain rather small subcatchments (Moorbach, Schl-Wehr, Lp1, Lp2; cf. Fig. 6). In addition, topsoil component scores clearly increased with discharge (Fig. 7). This is consistent with the observation that near-surface runoff constitutes a major fraction of stormflow runoff in both catchments (Buzek et al. 1995, Lischeid et al. 2002).

Long-term Patterns

Time series of solute concentration and of component scores of most of the sampling sites exhibited substantial short-term variation. Abstracting from that short-term dynamics the long-term pattern of component scores was remarkably similar at different sites. In general, the Lehstenbach and Lysina sampling sites can be split into three groups. The first group consists of the Lysina streams Lp1 and Lp2 and the Lysina upslope spring Lenka with nearly linear long-term patterns. The second group comprises the Lehstenbach deep groundwater wells with more cyclic long-term patterns. The Lehstenbach catchment runoff and the Lehstenbach upslope spring Schl_Wehr form a third group, exhibiting features of both groups. This grouping is likely to reflect the effect of increasing damping with depth which is the least pronounced for the first group and the most distinct for the second.

The long-term decrease of the first and fourth component at the Lysina sampling sites reflects in the first place the decrease of sulfur and nitrogen deposition. This effect can hardly be seen at the Lehstenbach deep groundwater wells. For the latters the interannual variability of climatic boundary conditions seems to be more decisive for the long-term redox conditions (Lischeid and Bittersohl 2008).

Beyond that, there was no clear relationship between low-pass filtered component scores and meteorological data. Only the topsoil component scores at the Lehstenbach streams Schl_Wehr, LB_Weir and the groundwater well GW04 seem to be related to the precipitation trend. However, a causal relationship is not very likely, as the latter exhibited the lowest topsoil component scores, and the LB_Weir rather low component scores (Fig. 6).

Solute Concentration versus Component Scores at the Lenka Site

Contrasting to all other Lehstenbach and Lysina sampling sites, there was a clear and almost linear decrease of NO_3^- concentration at the Lysina upslope spring Lenka since the end of the 1980s. This trend started almost ten years before nitrogen deposition started to decrease at that site, and a few years before SO_4^{2-} concentration started to decrease. In contrast, time series of the component scores at this site do not differ from those at other sites in the Lysina or Lenka catchment. Based on the results of this study, the apparently simple and intriguing trend of NO_3^- concentration seems to be the effect of the interplay of different processes that add to the observed long-term pattern (Fig. 16). It is well accepted that the concentration of a single solute is usually due to a variety of different processes. On the other hand, simple long-term patterns are usually ascribed to a single dominant process. This study followed an alternative approach. It is concluded that investigating time series of components as representations of single processes instead of analyzing time series of concentrations of single solutes was successful in resolving some of the apparent inconsistencies of the latter.

6. Summary and Conclusions

The objective of this study was to identify the prevailing biogeochemical processes that affected groundwater and stream water quality in two similar forested catchments at numerous sites, to investigate spatial patterns of processes, and to determine the long-term behaviour with respect to these processes. A non-linear principal component analysis of long-term groundwater and streamwater solute concentration data was performed to identify the dominant processes, and to investigate common long-term patterns in this region. The first four components could be ascribed to different processes and could be used as quantitative measures of the effect of these processes. Among these, only contamination by road salt was restricted to a few sites of the Lehstenbach catchment whereas the remaining three components and the associated processes had clear impacts in both catchments. The impact of topsoil solution infiltration could clearly been seen during major rainstorms and snowmelt. Redox processes seem to play a major role even in the oxic aquifer in both catchments which showed a seasonal pattern at various sites. The fourth component was interpreted as a sulfate contamination component which was less variable in the short-term at most sites. The approach allowed investigating the different effects and their long-term behaviour separately. Long-term behaviour determined by low-pass filtering of the time series of component scores showed consistent trends. The dominant source of different behavior at different sites seemed to be the varying thickness of the regolith and the fraction of wetland areas in the respective subcatchments. In the Lehstenbach deep groundwater wells long-term oscillations of single components were found whereas linear trends prevailed in the Lysina streams.

The analysis highlighted the relationship between different processes, namely an antagonism between NO_3^- and SO_4^{2-} concentration that adds to their common dependence on redox conditions. This

differentiation yielded a more clear and consistent picture than analysis of time series of single solutes. It is concluded that investigating spatial and temporal patterns of ”processes“ (components) is more promising than looking at single solutes.

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Study 2

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Catchments as heterogeneous and multi-species reactors: An integral approach for identifying biogeochemical hot-spots at the catchment scale

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Chemical variability

SUMMARY

From a biogeochemical perspective, catchments can be regarded as reactors that transform the input of various substances via precipitation or deposition as they pass through soils and aquifers towards draining streams. Understanding and modeling the variability of solute concentrations in catchment waters require the identification of the prevailing processes, determining their respective contribution to the observed transformation of substances, and the localization of "hot spots", that is, the most reactive areas of catchments.

For this study, we applied a non-linear variant of the Principle Component Analysis, the Isometric Feature Mapping (Isomap), to a data set composed of 1686 soil solution, groundwater and stream water samples and 16 variables (Al, Ca, Cl, Fe, K, Mg, Mn, Na, NH_4, NO_3, SO_4, total S, Si, DOC, electric conductivity and pH values) from the Lehstenbach catchment in Germany. The aim was (i) to assess the contribution of the prevailing biogeochemical processes to the variability of solute concentrations in water samples taken from soils, in groundwater and in stream water in a catchment and (ii) to identify hot spots at the catchment scale with respect to 16 solutes along different flow paths.

The first three dimensions of the Isomap analysis explained 48%, 30% and 11%, respectively, i.e. 89% of the variance in the data set. Scores of the first three dimensions could be ascribed to three predominating bundles of biogeochemical processes: (i) redox processes, (ii) acid-induced podzolization, and (iii) weathering processes.

In general, the upper 1 m topsoil layer could be considered as hot spots along flow paths from upslope soils and in the wetland, although with varying extents for the different prevailing biogeochemical processes. Nearly 67% and 97% of the variance with respect to redox processes and acid induced podzolization could be traced back to hot spots, respectively, representing less than 2% of the total spatial volume of the catchment. In contrast, biogeochemical processes in deep groundwater had only minor effects on the biogeochemical turnover in catchment waters. Hot spots with respect to weathering processes along upslope and wetland flow paths could not be quantified due to effects of preferential sampling in soil solution samples. Predominating flow paths and biogeochemical processes crucial for the variability of stream water chemistry differed substantially for three streams but were consistent with presumed mixing ratios.

1. Introduction

Catchments can be regarded as reactors for various dissolved organic and inorganic substances. Rainwater, fog, snow melt water and dissolved solutes infiltrate the soil or run off the soil surface on their way towards receiving streams (Neal et al., 1997; Stutter et al., 2006). Extensive field work and modeling studies have shown that subsurface water follows distinct flow paths rather than becomes completely mixed, even in shallow soil catchments (Biggs et al., 2006; Church, 1997; Hill, 1990; Rademacher et al., 2005). Along these flow paths a variety of biogeochemical processes occur that modify solute concentration (Biggs et al., 2006; McClain et al., 2003; Soulsby et al., 1998; Yang et al.,

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2012). Attempts have been made to better understand and to model the interplay of these processes (Church, 1997; McClain et al., 2003; Stutter et al., 2006) and to relate them to the catchment's structure and properties (Biggs et al., 2006; Church, 1997; Grathwohl et al., 2013; Stutter et al., 2006) as well as to determine anthropogenic impacts (Church, 1997; Foster et al., 2001; Krám et al., 1999; Vidon et al., 2010).

Single flow paths differ substantially from each other in transport velocity, travel time, and geochemical properties of the matrix (Botter, 2012; Liu et al., 2008; McDonnell et al., 2010; Neal et al., 1997; Yang et al., 2012) and are therefore exposed to a variety of processes. Changes of solute concentration along single flow paths depend on the respective process kinetics relative to exposure times (Oldham et al., 2013, and references therein) and to the concentration of reagents (McClain et al., 2003), on the density of reactive sites (e.g. Chapman et al., 1997; Church, 1997; Stutter et al., 2012, and references therein), and on redox conditions (e.g. Cirmo and McDonnell, 1997; Olivie-Lauquet et al., 2001; Paul et al., 2006). Consequently, there will be hot spots along the flow paths where solute concentration changes more rapidly over time, or on shorter distances, compared to other zones. Such hot spots can exist on different spatial scales, from molecular to global, depending on the system of interest (McClain et al., 2003) and can be responsible for a large part of the material turnover in aquatic ecosystems (Vidon et al., 2010). Hot spots are frequently described in terms of processes linked to the nitrogen or carbon cycle (Andrews et al., 2011; Groffman et al., 2009a; McClain et al., 2003; Vidon et al., 2010). Hot spots of organic matter mineralization were found to be important in the regulation of many biogeochemical cycles in riparian zones, as pointed out by Vidon et al. (2010). Groffman et al. (2009a) demonstrated that a high percentage of the denitrification activity in ecosystems occurs in hot spots, which in turn leads to a high uncertainty in denitrification models (Groffman et al., 2009b). Thus, understanding and modeling biogeochemical processes in catchments would benefit a lot from a systematic identification and characterization of these hot spots (Groffman et al., 2009a; McClain et al., 2003; Vidon et al., 2010). Otherwise, hot spots are often linked to the presence of multiple reactants that depend on the interplay of different biogeochemical processes (McClain et al., 2003; Vidon et al., 2010). However, up to now, researchers typically do not simultaneously study hot spots for multiple chemical species.

This study aims at testing an integral approach for (i) assessing the contribution of the prevailing biogeochemical processes to the variability of solute concentrations in water samples taken from soils, in groundwater and in stream water in a catchment, and (ii) identifying hot spots at the catchment scale with respect to 16 different solutes along different flow paths. We have performed a statistical analysis of the chemical composition of soil pore-water, groundwater and stream water from a forested catchment using the Isomap technique. Isomap is a non-linear variant of the Principal Component Analysis (Tenenbaum et al., 2000) which has been used previously to identify the prevailing biogeochemical processes responsible for the observed chemical composition of groundwater and stream water (Lischeid and Bittersohl, 2008; Lischeid et al., 2010), and of soil pore-water (Schilli et al., 2010), focusing in both studies on long-term patterns of water chemistry. In contrast, in this study spatial patterns in soil solution, groundwater and stream water chemistry were investigated. In natural systems linear structures often are more an exception rather than the rule (Mahecha et al., 2007; Ramette, 2007; Harris and Heathwaite, 2011), for example for most of the chemical reactions involved in the acidification process (Neal, 1997). Thus, the interpretation of the results of the linear PCA is often complicated (James and McCulloch, 1990; Lischeid and Bittersohl, 2008).

2. Study area

The Lehstenbach watershed is located in the Fichtelgebirge Mountains in southeast Germany (Gerstberger et al., 2004) at 50°08′N and 11°52′E. The watershed area is 4.19 km^2 and the elevation ranges from 690 to 877 m a.s.l. (Fig. 1). The bedrock consists of granite. The thickness of the regolith is up to 40 m and more. Dystric cambisols and podzols predominate. Fibric histosols and dystric gleysols are found in the riparian zone, representing about one third of the watershed area (Küsel and Alewell, 2004). The area is drained by a dense network of natural streams and artificial channels (Lischeid et al., 2002). Dense Norway spruce stands (*Picea abies*) cover more than 95% of the watershed area. Annual mean air temperature is 5.3 °C, and the annual mean precipitation is 1,162 mm (1971–2000 period) (Gerstberger et al., 2004). Snow pack usually develops in January, and final snow melt occurs in March (Lischeid et al., 2002).

Groundwater circulates mainly in the regolith which can be considered a porous aquifer with a saturated hydraulic conductivity of $3{\cdot}10^{-6}$ m s^{-1}. Mean residence time of water measured at the catchment outlet is 3.6 years (Lischeid et al., 2002). In the riparian zone, mean groundwater level is close to the surface during the whole year and more than 10 m below the surface in the upper part of the catchment.

Annual mean runoff was 470 mm during the period from 1991 to 2001 (Lischeid et al., 2010). Groundwater flow in the regolith parallel to the stream at the catchment outlet is likely to be a negligible portion of the total outflow (Lischeid et al., 2002). Stream discharge is generated by deep groundwater discharge during base flow conditions and does not fall below 0.25 mm per day, even during longer dry periods. During heavy rainstorms, the riparian zone is saturated up to the surface, thus hydrologically connected to the stream which can explain the strong increase (by a factor of 10–20 compared to base flow) in stream discharge during heavy rainstorms (Lischeid et al., 2002).

The watershed is still highly affected by atmospheric depositions (sulfur oxides, nitrogen oxides, protons, base cations) that peaked in the 1970s and steadily decreased thereafter (Matzner et al., 2004). In general, Ca and Na are the predominating cations in streams and groundwater (Lischeid et al., 2004). The waters are acid and mostly hydrogen carbonate-free with a pH between 3.3 and 6.

3. Methods

3.1. Sampling and chemical analysis

Soil solution, groundwater and stream water samples were taken along different flow paths in the catchment. Water flow paths have not been determined directly. They were delineated based on the results from previous studies in this catchment (Lischeid et al., 2002; Lischeid et al., 2004). Water samples were analyzed for different chemical variables. The sampling strategy was chosen with the aim to sample all water compartments relevant to assessing the chemical evolution along the different flow paths: flow paths from upslope soils to an upslope spring, from upslope soils to the catchment outlet, and wetland flow paths (Fig. 2). Sampled water compartments were chosen along the flow paths: soil solution from upslope soils and from the wetland, i.e. close to the input boundary; groundwater from upslope sites and from the wetland, and water from an upslope spring, the Moorbach stream and the eastern tributary of the Lehstenbach stream, representing solute output from the upslope sites, the wetland site and the catchment, respectively. It was assumed that these sampling sites represented to a sufficient degree the different water

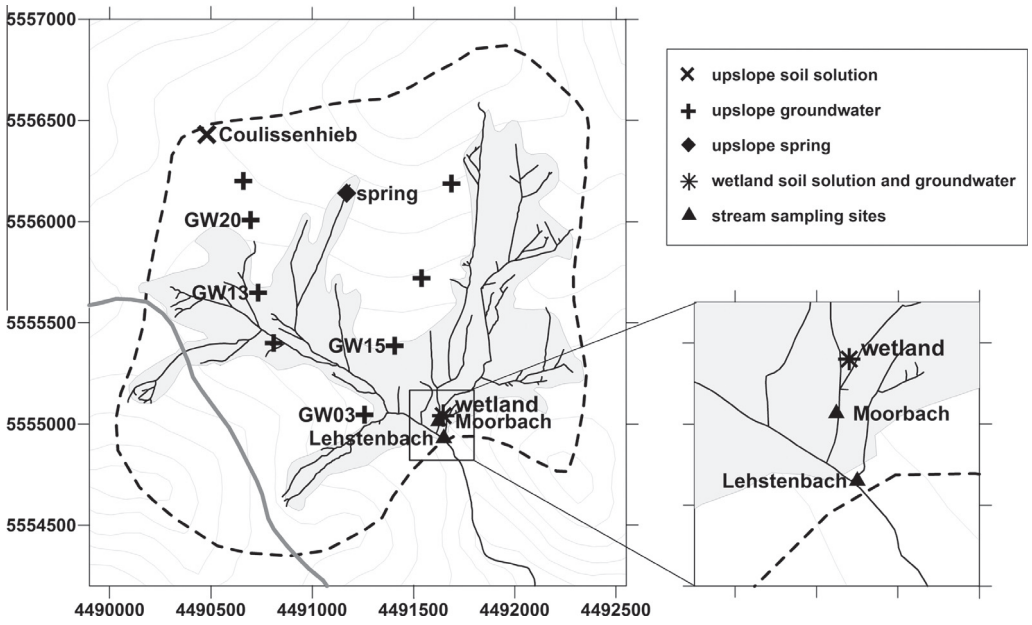

Fig. 1. Map of the Lehstenbach watershed in the Fichtelgebirge Mountains in southeast Germany and sampling sites. Gauss-Krüger coordinates [m] are given at the axes. Black symbols: sampling sites; black dashed line: catchment border; black solid lines: streams; solid gray line: public road; gray area: riparian zone. At the sampling sites GW03, GW13, GW15 and GW20, 1 (GW15) or 2 (GW03, GW13, GW20) additional piezometers were installed at different depths.

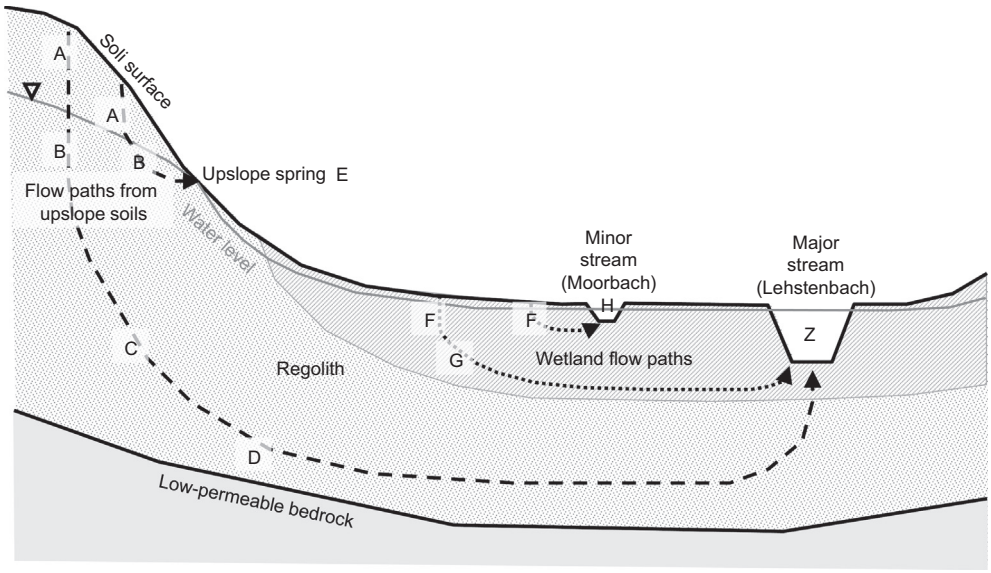

Fig. 2. Scheme of the flow paths from upslope soils and of the wetland flow paths. Letters A–H and Z correspond to the sampled water compartments along the different flow paths. Flow paths from upslope soils (A-B-E and A-B-C-D-Z): A: upslope soil solution sampled in 0.03 m, 0.2 m and 0.9 m depth and shallow groundwater sampled at upslope sites in 0.9 m depth, B: shallow groundwater sampled at upslope sites between 1.9 m and 3.2 m, C: deep groundwater sampled at upslope sites at 10 m or 10.7 m depth, D: deep groundwater sampled at upslope sites at 16 m depth or deeper, E: surface water from the upslope spring. Wetland flow paths (F-H, F-G-Z): F: wetland soil solution sampled in 0.1 m, 0.2 m and 0.4 m depth and shallow groundwater sampled at the wetland site in 0.4 m depth, G: shallow groundwater sampled at the wetland site in 1 m depth, H: surface water from the Moorbach stream. Z: surface water from the catchment outlet, i.e. the Lehstenbach stream.

compartments in the catchment. Note, that "upslope sites" summarizes all soil solution and groundwater sampling sites outside the wetland area, i.e. groundwater sampling sites with oxic groundwater.

Sampling was carried out between March 2005 and April 2008 (Table 1). Samples were taken at 9 upslope sites (Coulissenhieb site, upslope groundwater sampling sites), the wetland site and 3 spring and stream water sampling sites (Fig. 1), mostly at monthly intervals at least. In total, the data set included 16 variables of 1686 samples: Al, Ca, Cl, Fe, K, Mg, Mn, Na, NH_4, NO_3, SO_4, total S, Si, DOC, electric conductivity, and pH values.

At the Coulissenhieb site, upslope soil solution was collected by 81 ceramic suction cups installed at 0.03, 0.2 and 0.9 m depth within nine plots. Three of the plots were subject to a freezing/thawing experiment (for more details see Muhr et al., 2008). Three samples from three plots were mixed to a composite sample for each depth, respectively. We assumed that upslope soil solution from the Coulissenhieb site represented to a sufficient degree the

Table 1
Atrribution of water samples to different sampling groups depending on the sampling depth of the water samples, number of samples included in the Isomap analysis, number of sampling dates and the sampling period for each sampling group. The sampling group "Lehstenbach stream" consists of samples from the eastern tributary of the Lehstenbach stream.

	Sampling group	Comprised of	Number of samples	Number of sampling dates	Sampling period
Flow paths from upslope soils	Upslope soils 0.03 m	Soil solution from organic layer	139	39	December 2005–April 2008
	Upslope soils 0.2 m	Soil solution	161	39	December 2005–April 2008
	Upslope soils 0.9 m	Soil solution and shallow groundwater	161	39 and 6, respectively	December 2005–April 2008 and October 2005–October 2007, respectively
	Upslope soils 2 m	Shallow groundwater sampled between 1.9 and 2.2 m depth	35	19	October 2005–October 2007
	Upslope soils 3.1 m	Shallow groundwater sampled between 3.0 and 3.2 m depth	31	19	October 2005–October 2007
	Deep groundwater 10 m	Deep groundwater sampled in 10 or 10.7 m depth	51	19	October 2005–October 2007
	Deep groundwater 16 m	Deep groundwater sampled in 16 m depth or deeper	17	16	October 2005–October 2007
Wetland flow paths	Wetlands 0.1 m	Soil solution	158	32	April 2006–February 2008
	Wetlands 0.2 m	Soil solution	135	32	April 2006–February 2008
	Wetlands 0.4 m	Soil solution and shallow groundwater	333	32 and 23, respectively	April 2006–February 2008 and November 2005–November 2007, respectively
	Wetlands 1.0 m	Shallow groundwater	154	23	November 2005–November 2007
Surface waters (Solute output)	Upslope spring		7	7	March 2005–July 2007
	Moorbach stream		282	282	April 2005–November 2007
	Lehstenbach stream		18	18	December 2005–October 2007

spatial variability found in the oxic soils in the catchment. Indeed, previous studies in the catchment showed that depth gradients of soil solution chemistry and the temporal variability largely exceeded the spatial variability between sampling sites (Schilli et al., 2010).

At the upslope groundwater sampling sites, groundwater samples were taken with a submersed pump in 8 observation wells screened down to at least 10 m depth, and with a maximal gauging depth of 26 m. At the sampling sites GW03, GW13, GW15 and GW20, one or two additional piezometers beside the observation well allowed sampling the groundwater at lesser depths (shallow groundwater). They were installed in 2.2 m and 3.2 m (GW03), in 2.0 m and 3.0 m (GW13), in 4.1 m (GW15), and in 0.9 and 1.9 m (GW20) below the surface. Spring water from the upslope spring near the catchment border was collected as grab samples.

The wetland site (Fig. 1) is a slightly acidic fen near the catchment outlet with an area of 0.08 km^2 (Reiche et al., 2009). The thickness of the peat layer on top of the mineral soil ranges between 30 and 70 cm. Soil solution from this wetland site was collected by 54 ceramic suction cups installed in 0.1, 0.2 and 0.4 m depth within six different plots. The ceramic cups operated at a continuous suction of −25 kPa. Three samples from three plots were mixed to a composite sample for each depth, respectively. A dense network of 36 piezometers at 0.4 m depth and at 1 m depth, respectively, was installed within the six plots for groundwater sampling using an air-tight vacuum system pump to prevent water from mixing with oxygen during sampling. Three of the six plots were subject to two drying/rewetting experiments in August and in September 2006, and from May to July 2007 (for more details see Reiche et al., 2009).

The wetland is drained by the ephemeral Moorbach stream. Stream water samples were taken with an automatic sampler at daily intervals. Samples taken during runoff events were selected and analyzed. Stream water samples from the eastern tributary of the Lehstenbach stream close to the catchment outlet were taken as grab samples, mainly during base flow conditions. Samples from the western tributary were not included because of contamination from road salt (Lischeid and Bittersohl, 2008). The portion of wetland areas in the (sub)catchments of the upslope spring, the Moorbach stream and the Lehstenbach stream was 0%, 100% and 35%, respectively. Along the different flow paths, water samples were attributed to different sampling groups depending on the sampling depth of the water samples as summarized in Table 1. Two upslope groundwater sampling sites were the only ones with a sampling depth of 4.1 and 26 m, respectively and, in addition, were sampled only once. Thus, although included in the Isomap analysis, the 2 water samples from these sites were not explicitly considered for the water sampling groups.

Soil solution, groundwater, spring water and water from the eastern tributary of the Lehstenbach stream were sampled at monthly intervals. Additional sampling campaigns were performed at the end of the drought period and after rewetting during both experiments at the wetland site for soil solution and groundwater sampling and for upslope soil solution sampling at the Coulissenhieb site.

Water and soil solution samples were filtered through a cellulose-acetate-membrane filter with 0.45 μm pore size. They were stored in polyethylene bottles in the dark at 2 °C until further analysis. Element concentrations of Al, Ca, Fe, K, Mg, Mn, Na, total S and Si were analyzed by ICP-OES (Varian Vista-Pro CCD Simultaneous). Cl, NO_3 and SO_4 were analyzed using ion chromatography (IC Dionex DX 500), DOC by temperature combustion and subsequent determination of CO_2 (Analytik Jena Multi N/C 2100 F), NH_4 by Flow Injection Analysis (FIA-LAB by MLE). Quality assurance of the data was performed prior to this study by the BayCEER central laboratory. Electric conductivity was measured with a TetraCon® 325 conductivity cell (WTW), pH values with a SenTix® 41-3 electrode (WTW).

3.2. Isometric Feature Mapping (Isomap)

The Isomap approach is based on classical multidimensional scaling (CMDS) (Tenenbaum et al., 2000). It has shown higher efficiency in representing the variance of a given data set compared to the linear Principal Component Analysis (PCA) (Tenenbaum et al., 2000; Mahecha et al., 2007). Geodesic distances between faraway points are estimated by summing up a sequence of euclidian distances between neighboring points in order to preserve non-linear

structures in the dataset. In a first step for every data point the k nearest neighbors are determined. The selection of k is based on a trial-and-error approach. Then, Isomap estimates the geodesic distances between all pairs of points by determining the smallest sum of the interpoint distances determined in the first step. In the last step, CMDS is applied to the estimated geodesic distances, projecting the nonlinear structures of the dataset onto a low-dimensional ordination space. The method is described in detail in Lee and Verleysen (2007).

Values less than the limit of quantization were replaced by 0.5 times that limit. Missing values were replaced by the mean of the respective parameter. The data were then normalized to zero mean and unit variance for each variable separately. All statistical analyses were performed using the R statistical software environment (R Development Core Team, 2006).

Each of the dimensions given by the Isomap analysis "represent" variables that are correlated with each other, irrespective of the type of relationship. These dimensions can be interpreted corresponding to the linear principal components. However, they are not necessarily linear. Thus, Spearman's rank correlation coefficients between single dimensions and variables were calculated. The variables with the highest Spearman coefficient with each single Isomap dimension were selected and considered to be the key variables for the dimensions. The Isomap analysis has been performed with the package "vegan" (Oksanen et al., 2007).

The performance of the Isomap approach was evaluated by the Pearson correlation between the interpoint distances in the high dimensional original data space with the interpoint distances in the low dimensional Isomap data space. The measure gives a value of one for a perfect fit, close to zero for a very poor fit, and is referred to as "explained variance" in the following.

The median of the dimension scores and the variance were calculated for each of the sampling groups for the first three Isomap dimensions in order to assess the macro scale variability of dimension scores along the different flow paths and the variability within one sampling group, respectively.

3.3. Quantifying the fraction of variance explained by hot spots

Considerable changes of the median of dimension scores on short distances along the flow paths were assumed to represent hot spots. These hot spots represent a certain fraction of the total variance of dimension scores explained by a certain Isomap dimension. The former was calculated using the difference between the minimum and the maximum median of dimension scores within a hot spot relative to the difference between the minimum and the maximum median of dimension scores of all water sampling groups, which was assumed to represent 100% of the variance explained by the Isomap dimension. Furthermore, these hot spots only constitute a fraction of the total spatial volume of the catchment. The latter was calculated using an assumed thickness of the regolith of 35 m, and the total catchment area of 4.19 km^2. The fractions of the hot spots were calculated using the thickness of the hot spot, the portion of the non-wetland (65% of 4.19 km^2) and the wetland area (35% of 4.19 km^2) in the catchment for the hot spots of upslope soils and of wetland soils, respectively, relative to the total spatial volume of the catchment. The quantification was realized for those hot spots that were identified in the results and the discussion section and could not be realized for all hot spots (see Section 5).

4. Results

4.1. Non-linear statistical analysis

The performance of the Isomap analysis depends on the choice of the parameter k, i.e. the number of neighbor points for determination of the geodesic distances (Tenenbaum et al., 2000). In our study, the best performance was found for k = 1190 by systematical variation of this parameter.

The first three Isomap dimensions represented about 89% of the variance (Fig. 3). Only the first three dimensions will be interpreted in this study that represented 48%, 30% and 11% of the variance of the interpoint distances of the data set, respectively. The 4th to 10th Isomap dimensions exhibited only minor contributions to the explained variance.

High scores of the 1st Isomap dimension were associated with high total S, SO_4, NO_3, Mn, K, Mg and Ca concentrations and with high electric conductivity values, low scores with high Fe and Si concentrations and high pH values (Fig. 4). Some relationships exhibited strongly non-linear patterns, e.g., electric conductivity or Fe concentration versus scores of the 1st dimension (Fig. 5). The 2nd dimension was positively correlated with DOC, Fe and Al, and negatively with total S, SO_4, Na and pH (Fig. 4). The 3rd dimension was characterized by positive loadings of Cl, Si, NH_4, K, Na and pH values and negative loadings of Al, total S and SO_4. Note that the total S nearly exclusively consists of SO_4 in waters of the catchment under study. Thus, only SO_4 is used for further interpretation of the data.

4.2. Changes of dimension scores along the flow paths

The scores of the first three Isomap dimensions varied systematically among the different sampling groups along each flow path (Fig. 6). Scores of the 1st dimension were considerably lower for the wetland flow paths compared to those from the upslope soils and decreased with depth in the wetlands (Fig. 6). Correspondingly, scores of the Moorbach stream with 100% wetland area in its catchment were the lowest, and those of the upslope spring without any wetland in its catchment were the highest, similar to those of the upslope soils (Fig. 6). In the deep groundwater of the upslope sites only a minor decrease of dimension scores was observed.

In contrast, both at the upslope soils and in the wetlands, considerable modifications of the scores of the 2nd and 3rd dimension were observed (Fig. 6), indicating hot spots in the uppermost soil horizons. In the upslope soils, scores of the 2nd dimension

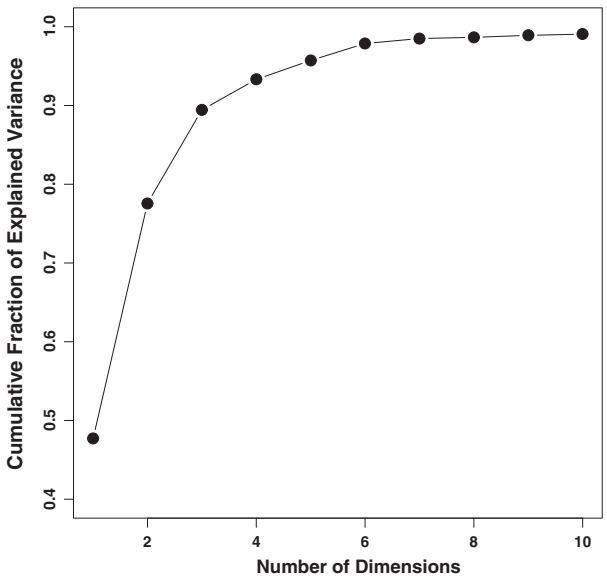

Fig. 3. Pearson correlation coefficients between the interpoint distances in the 18-dimensional data space and in the low-dimensional projection, referred to as "explained variance", for the first 10 Isomap dimensions.

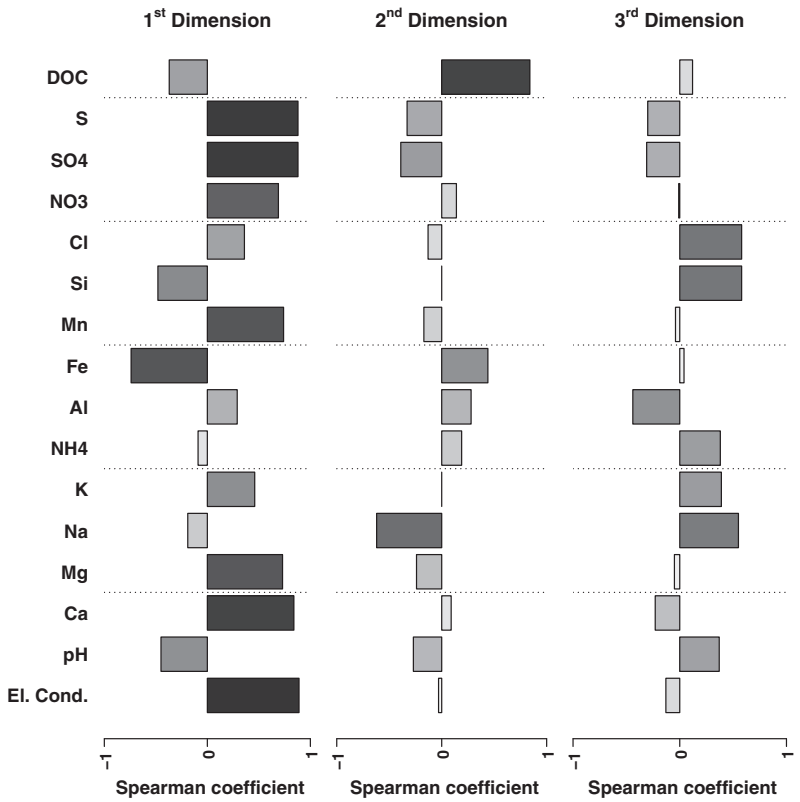

Fig. 4. Spearman coefficients (ρ) between the analyzed variables and the first three Isomap dimensions. Gray shading is proportional to Spearman ρ. El. Cond.: electric conductivity.

decreased down to a depth of 3 m with a sharp decrease within the uppermost 0.9 m soil layer, and leveled off in the deep groundwater at greater depth. Along the wetland flow paths, scores of the 2nd dimension were around 0 for the first 40 cm, i.e., within the peat layer, and then decreased down to 1 m depth. Similar to the 1st dimension, scores of the 2nd dimension were considerably lower for the wetland topsoil than those for the upslope topsoil. Among the stream water samples, those of the Moorbach stream exhibited the highest scores, whereas those of the upslope spring and of the catchment runoff were almost identical.

Along the flow paths from the upslope soils, scores of the 3rd dimension decreased down to 0.9 m depth and then increased again down to 16 m depth, whereas along the wetland flow paths a clear increase of scores was observed. Among the three streams, the catchment runoff exhibited the highest values of the scores of the 3rd dimension, and the upslope spring the lowest.

For all three dimensions, the scores of all three streams were always within the range of soil solution and groundwater sampling groups (Fig. 6). Scores of the 1st dimension for the upslope spring were in the same range as was found for upslope soil solution samples, scores of the 2nd and 3rd dimension in the range of upslope soil solution in 0.9 m depth, and of shallow groundwater in 2 m depth.

4.3. Quantifying the fraction of variance explained by hot spots

Based on the results and the discussion (see Section 5) of the hot spots, the fraction of variance explained by hot spots was calculated for the uppermost 0.1 m soil layer in the wetlands with respect to the 1st and the 2nd Isomap dimension and for the first 0.9 m of flow paths from upslope soils with respect to the 2nd dimension. Results are given in Table 2. The corresponding fractions of the spatial volume represented by these hot spots are given in Table 3.

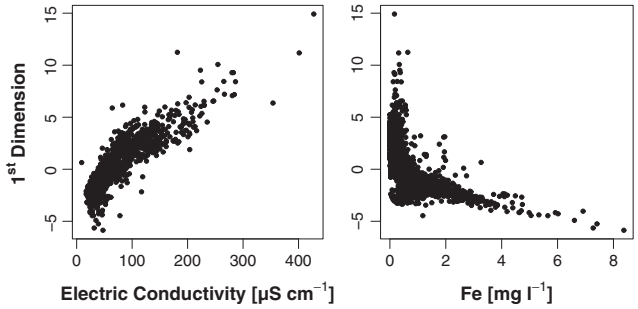

Fig. 5. Scatter plots of the 1st Isomap dimension (*y*-axis) versus electric conductivity [µS cm^{-1}] and Fe concentrations [mg l^{-1}] (*x*-axis).

5. Discussion

5.1. Process identification using the Isomap approach

Differing solute concentrations in water samples reflect reactions that occurred along the flow paths. The Isomap analysis revealed some very strong relationships between dimension scores and the concentration of specific constituents. This observation implies the following biogeochemical interpretation: Dimensions reflect characteristic chemical signatures generated by a variety of biogeochemical processes, provided that the water volume's exposure time to the respective biogeochemical processes is clearly longer then its characteristic reaction time. Only then will these processes exert an imprinting effect on the chemical

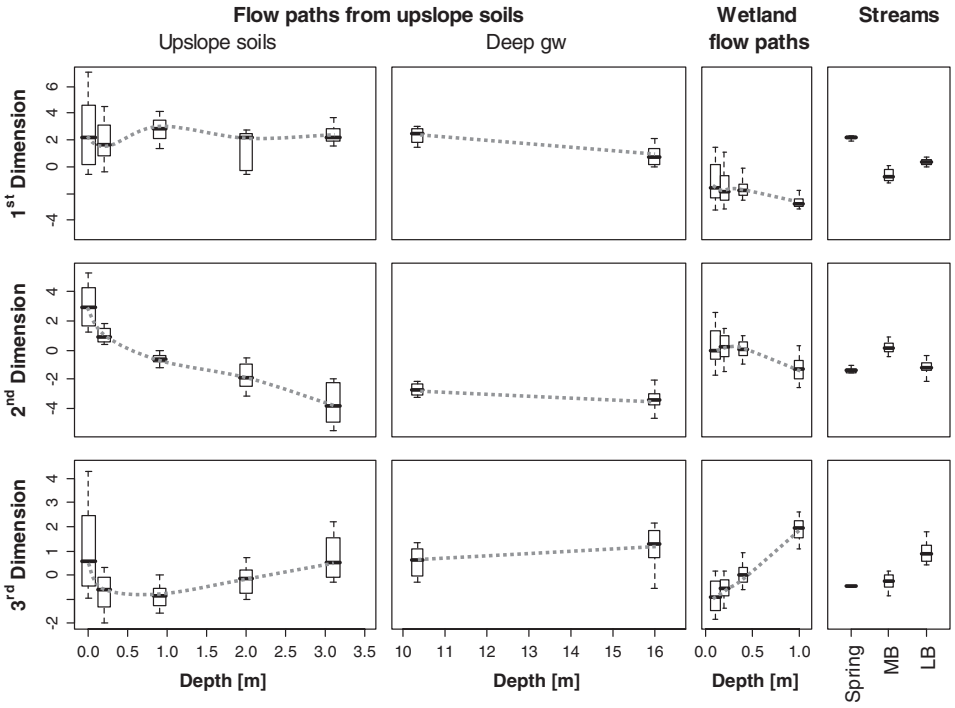

Fig. 6. Median of dimension scores for different sampling groups vs. sampling depth for the first three Isomap dimensions for different flow paths. Crossbars represent median values of dimension scores; boxes are representative for the variance of the dimension scores, and the whiskers give the 10% and 90% confidence intervals. Samples from the upslope soils at 0.9 m depth comprised soil solution and shallow groundwater samples. Samples from upslope soils at 2 and 3.1 m depth were groundwater samples taken between 1.9 and 2.2 m depth and between 3.0 and 3.2 m depth, respectively, and have been grouped for better visibility. Samples from the wetland sites at 0.4 m depth comprised soil solution and shallow groundwater samples. Spring: Upslope spring, MB: Moorbach stream, LB: eastern tributary of the Lehstenbach stream.

composition of water samples (Oldham et al., 2013). Such preconditions are met at locations in the catchment where boundary conditions for the respective biogeochemical processes are favorable, depending on the concentration of reactants and the chemical state (e.g., redox state, pH, or ionic strength; Cirmo and McDonnell, 1997; Lohse et al., 2009). It is assumed that this creates the observed statistical variability of dimension scores. Based on these considerations, we attempt in the following to identify biogeochemical processes characteristic for each of the three dimensions.

5.1.1. First Isomap dimension

High scores of the 1st Isomap dimension were associated with high SO_4, NO_3, Mn, K, Mg and Ca concentration and electric conductivity values, low scores with high Fe and Si concentration and pH values (Figs. 4 and 5). A similar combination of variables correlated with the 1st dimension was found by Schilli et al. (2010) for a soil solution data set from the same catchment. They interpreted the dimension to represent geochemical signatures influenced by atmospheric deposition. Indeed, SO_4, NO_3, Ca, Mg and K originate from atmospheric deposition which played a major role for the biogeochemical functioning of many forested catchments (Matzner et al., 2004 and references therein). On the other hand, the correlation of SO_4, NO_3, Fe, Si and pH with an Isomap dimension in a groundwater data set from the same catchment has been interpreted to represent signatures affected by redox processes (Lischeid and Bittersohl, 2008). In fact, SO_4, NO_3, Mn and Fe are redox sensitive variables. There seems to be a threshold value for scores of that dimension of about 0 with a substantial increase of Fe concentration below (Fig. 5) which could indicate reduced conditions. Due to technical constraints of the soil suction cups, neither oxygen concentration data nor measurements of redox potential were available which could have confirmed this interpretation.

Redox processes like nitrification, denitrification, Fe oxidation and reduction as well as SO_4 reduction and sulfide oxidation processes have been identified to be relevant at the upslope sites (e.g. Alewell and Gehre, 1999; Durka et al., 1994; Hentschel et al., 2007) and in the wetlands of this catchment (Alewell et al., 2006; Knorr et al., 2009; Küsel and Alewell, 2004; Paul et al., 2006). Indeed, high dimension scores, corresponding to high concentrations of SO_4 and NO_3, were found mainly for oxic environments (i.e. the upslope soils and deep groundwater) whereas low dimension scores with high Fe and Si concentrations and high pH values were found mainly for anoxic environments (i.e. the wetlands). The higher pH values were in line with H^+ consumption during reduction processes. Higher Si concentrations could be due to "old" groundwater discharge in the wetlands as was argued by Lischeid and Bittersohl (2008).

The high correlation of with the 1st dimension has to be interpreted with caution. This correlation was mainly determined by high Mn concentrations found in newly installed groundwater wells at the upslope sites (data not shown). These high concentrations clearly decreased with time since then. It is likely that Mn in the bentonite sealing was released due to drilling (Lischeid and Bittersohl, 2008) and will therefore not be discussed further. Presumably, K, Mg and Ca could be released from the bentonite sealing as well. However, in contrast to Mn, high concentrations of these solutes were not restricted to the newly installed groundwater wells but were found also in numerous soil solution samples without any contact to a bentonite sealing. Ammonium was not correlated with the 1st dimension (Fig. 4), although it originated from atmospheric deposition and mineralization processes as well. This was likely due to the occurrence of NH_4 in only one single sampling group, i.e. the upslope topsoil layer, due to sorption to clay minerals and oxidation in deeper soil layers.

We conclude that high scores of the 1st dimension characterize soil solution, groundwater and stream water which exhibits high

Table 2
Relative quantification of the identified hot spots with respect to the 1st and 2nd Isomap dimension, representing redox processes and acid-induced podzolization processes, respectively. Sampling group: sampling groups representing the minimum and maximum median of dimension scores of all sampling groups in the catchment or of the hot spot, respectively. For calculating the difference between the minimum and the maximum median of dimension scores within the hot spot in the uppermost 10 cm layer of the wetland soils the median of the upslope soils in 0.03 m depth was used. It was assumed that this value is nearest to the input signal (open field precipitation and throughfall) for both the flow path from upslope soils and the wetland flow paths. The fraction of variance explained was calculated as the ratio between the difference between the minimum and the maximum median of dimension scores for the hot spot, and the difference between the minimum and maximum median of dimension scores of the whole catchment.

Isomap dimension/biogeochemical process bundle		Sampling group	Maximal and minimal median of dimension scores, respectively	Difference between maximal and minimal median of dimension scores	Fraction of variance explained (%)
1st dimension: redox processes	Whole catchment	Upslope soils 0.9 m Wetland soils 1 m	2.79 −2.75	5.54	100
	Hot spot wetland 0.1 m	Upslope soils 0.03 m Wetland soils 0.1 m	2.17 −1.54	3.71	66.8
2nd dimension: acid-induced podzolization	Whole catchment	Upslope soils 0.03 Upslope soils 3.1 m	2.96 −3.80	6.76	100
	Hot spot upslope soils 0.9 m	Upslope soils 0.03 m Upslope soils 0.9 m	2.96 −0.59	3.55	52.5
	Hot spot wetland 0.1 m	Upslope soils 0.03 m Wetland soils 0.1 m	2.96 0.01	2.95	43.7

Table 3
Fraction of the catchment's spatial volume represented by the identified hot spots with respect to the 1st and 2nd Isomap dimension, representing redox processes and acid-induced podzolization processes, respectively.

Isomap dimension/ biogeochemical process bundle		Thickness of the regolith/hot spot (m)	Fraction of catchment area (non-wetland/wetland)	3-D domain (km^3)	Fraction of 3-D domain of the whole catchment (%)
	Whole catchment (4.19 km^2)	35		0.14665000	100
1st dimension: redox processes	Hot spot wetland 0.1 m	0.1	0.35	0.00014665	0.1
2nd dimension: acid-induced podzolization	Hot spot upslope soils 0.9 m	0.9	0.65	0.00245115	1.7
	Hot spot wetland 0.1 m	0.1	0.35	0.00014665	0.1

concentration of NO_3, SO_4 and accompanying cations under oxic conditions, whereas low scores represent samples from highly reduced environments. For the sake of clarity, this dimension will be referred to as "redox" dimension hereafter, although this is certainly a simplification of a bundle of related processes.

5.1.2. Second Isomap dimension

The positive correlation between DOC, Fe and Al, and the scores of the 2nd dimension as well as the negative correlation with pH values (Fig. 4) is a typical signature for podzolization processes (Lundström et al., 2000). This interpretation follows the reasoning of Schilli et al. (2010), who found similar results for a soil solution data set of the Lehstenbach catchment. Scores of the 2nd dimension were the highest at shallow depth at the upslope soils (Fig. 6) reflecting the high values of DOC, Fe and Al in the forest floor and the accumulation horizons (Bh, Bs) of the podzol in about 20 cm depth. Scores decreased with depth, which can be interpreted by observations made in previous process studies in the catchment. Decreasing DOC, Fe and Al concentrations with increasing depth in the podzols of the catchment were attributed to microbial decay, sorption of DOC onto Fe and Al oxides/hydroxides, and (co)precipitation with Fe and Al (Kalbitz and Kaiser, 2008; Kalbitz et al., 2004).

Low scores of that dimension came along with enhanced SO_4 and Na concentrations and higher pH values as were found in the deeper layers of upslope soils (shallow groundwater) and in deep groundwater (Fig. 6). The high SO_4 concentrations would be consistent with the acidifying effects of high sulfur deposition mainly during the 1960s and 1970s (Matzner et al., 2004). The location of which now has moved to a few m depth (Lischeid, 2001; Lischeid et al., 2004), having enhanced podzolization processes in the upper soil layers in the past and mineral weathering in the deeper soil layers (Huang et al., 2013; Maitat et al., 2000), reflected by high SO_4 and Na concentrations and higher pH values found in shallow and deep groundwater samples. In fact, Na mainly originates from hydrolysis of feldspars (Weyer et al., 2008) occurring predominantly at greater depths in the deeply weathered granitic bedrock (Lischeid et al., 2002). A negative correlation between DOC and SO_4 has been found in numerous streams across North America and northern and central Europe, simultaneously with the decline of SO_4 deposition in these regions (Borken et al., 2011; Monteith et al., 2007).

Denitrification and sulfide oxidation in the wetlands increase the alkalinity (Alewell and Matzner, 1993; Lindemann, 1997). Thus, acid-induced podzolization is not that relevant for the wetland site with fibric histosols and dystric gleysols. Correspondingly, the scores of the 2nd dimension in the peat layer of the wetland site (down to 0.4 m depth) were lower compared to those of the upslope soils (Fig. 6). To conclude, this dimension seems to reflect chemical signatures affected by acid-induced podzolization and associated reactions.

5.1.3. Third Isomap dimension

High scores of the 3rd dimension were found in the forest floor and in the deeper layers of upslope soils (shallow groundwater), in the deep groundwater, and in the deeper layers at the wetland site

and were associated with higher values of Na, Si, NH_4, K, Cl and pH. Low scores were observed in waters sampled at 0.2 and 0.9 m depth of upslope soils and at 0.1 m depth at the wetland site and were associated with high values of Al and SO_4 (Figs. 4 and 6).

Silicon and Na originate mainly from silicate weathering in deeper layers of the catchment (Weyer et al., 2008) which was in line with the high scores in shallow and deep groundwater (Fig. 6). The same holds true for the deeper layers at the wetland site, where high clay content was found.

High dimension scores were also found in the organic layer of the topsoil of upslope soils where silicate weathering is an unlikely process. Instead, base cation release by cation exchange was indicated by the correlation of the third dimension with NH_4 and K that originate from atmospheric deposition or internal cycling of organic matter. Simultaneously, Cl was also positively correlated with the 3rd dimension, mainly originating from atmospheric deposition as well (Matzner et al., 2004).

The correlation between high scores of the 3rd Isomap dimension and higher pH values point to silicate weathering and cation exchange as predominating buffering systems in the soil and seems to corroborate weathering as the key process for the chemical signature reflected by this dimension.

Soil acidification caused by high sulfur deposition up to the 1980s (Matzner et al., 2004) lead to high SO_4 concentrations and Al saturation of more than 97% of the cation exchange capacity in the mineral soil of this catchment (Gerstberger et al., 2004), indicating weathering of Al containing minerals as buffering system in these soil layers. In contrast to the release of Na and Si via silicate weathering (represented by positive dimension scores), Al releasing weathering reactions require lower pH values as was found in the soil layers between 0.2 and 0.9 m depth (negative dimension scores). Similar to the upslope soils, low scores and high Al and SO_4 concentration were found in the topsoil at the wetland site (Fig. 6). Although SO_4 originates from atmospheric deposition like Cl, SO_4 is negatively and Cl positively correlated with the 3rd dimension. Aluminum in soil solution was often shown to be related to strong mineral acid anions like SO_4 (e.g. Dise et al., 2001), whereas a similar correlation between SO_4 and Cl was not observed. The lack of correlation between Al and DOC with respect to the 3rd dimension is likely due to the large C pool in the peat layer that likely did not change due to Al dynamics.

We propose that the chemical signature represented by the 3rd dimension reflects the release of base cations, Si and Al via silicate weathering and cation exchange which had been intensified by high sulfur deposition. To give a concise label, it will be referred to as the weathering dimension in the following discussion.

5.2. Hot spots of biogeochemical transformation along flow paths

A change of Isomap dimension scores along the flow paths was assumed to indicate a change of the respective contribution of the biogeochemical transformation processes, resulting in a change of solute concentrations. Flow paths have not been determined directly, but it was assumed that seepage flux in the unsaturated zone was vertical and that groundwater flow was horizontal. This presumably holds true for shallow groundwater in the wetlands (Fig. 2). Thus, the gradients of dimension scores over depth in the unsaturated zone cannot be compared directly with those in the deep groundwater and at the wetland site. In addition, transport velocity presumably differs between the different sampling sites and sampling depths and will not be constant in time. Thus, our results do not allow direct inference of transformation rates of different processes. Nevertheless, zones of major change of dimension scores on short distances likely represent the most reactive areas of the catchment with respect to these processes.

5.2.1. First Isomap dimension

The chemical signature described by the 1st dimension seems to be hardly modified in the unsaturated zone of the upslope soil and aquifer as it remained constant throughout the entire catchment except in wetlands (Fig. 6). In contrast, in wetland soils a sharp decrease of oxygen concentrations is typically found within the upper 10 cm of wetland soil profiles in the Lehstenbach catchment (Knorr et al., 2009), pointing to a considerable impact of anoxic mineralization processes. In fact, despite the same input signal (open field precipitation and throughfall), the scores of the 1st dimension for the wetland topsoil were lower than those for the upslope topsoil. This suggests that the uppermost 10 cm layer of the wetland soils had a major impact on the chemical composition of the water with respect to the redox processes. In fact, the highest rates of Fe(II) formation and SO_4 consumption were found between 0 and 10 cm depth in anoxic microcosm experiments (Küsel et al., 2008). Below 10 cm depth, scores of the 1st dimension decreased only slightly. Thus, the uppermost 10 cm layer of the wetland soils can be considered as a major hot spot that accounts for the largest fraction of biogeochemical turnover by redox processes.

5.2.2. Second Isomap dimension

Scores of the 2nd dimension decreased down to 3 m depth with a sharp decrease within the uppermost 0.9 m layer at the upslope sites (Fig. 6). Correspondingly, scores of the 2nd dimension decreased with depth in wetland soils. It is remarkable that scores at 0.9 m depth are about the same in upslope and wetland soils, whereas those at 10 cm depth were clearly lower in the wetland soils compared to the upslope soils. As has been observed for the 1st dimension, the uppermost 10 cm layer of the wetland soils seems to play a major role for acid-induced podzolization processes associated with the 2nd dimension. In fact, the top of the small hummocks in the wetland was not permanently water saturated which likely lead to at least temporary oxic conditions (Frei et al., 2010). Likewise, the oxic topsoil layer at another wetland site in the same catchment was saturated only during single rainstorms and snowmelt events (Lischeid et al., 2007).

The impact of podzolization processes seems to be restricted to the uppermost 3 m layer at the upslope sites. This pattern may have been amplified by the acidifying effects of historical high sulfur deposition, the location of which has now moved to a few m depth (Lischeid, 2001; Lischeid et al., 2004; Matzner et al., 2004), enhancing podzolization and mineral weathering.

5.2.3. Third Isomap dimension

In the wetland soils, a continuous increase of scores of the 3rd dimension down to 1 m depth (Fig. 6) points to a considerable change of the chemical state affecting processes related to weathering and cation exchange. However, at the upslope sites, a corresponding increase of scores with depth is restricted to depths below 0.9 m, and is tending to level off at greater depths in the aquifer. In contrast, there is a clear decrease of scores from the topsoil down to 0.9 m depth, which is exactly the opposite of the pattern found in the wetland soil (Fig. 6).

This contradicts the assumption of an approximately monotonous transformation of solute concentration along the flow path. There is some evidence that samples from suction cups at different depths may not represent a continuum of the same flow path, but rather the immobile fraction of soil solution (Brandi-Dohrn et al., 1996; Landon et al., 1999). The immobile fraction is characterized by a rather long residence time. In addition, the immobile soil water fraction is located more in small diameter pores with a large interface between soil solution and soil matrix. This immobile fraction interacts with the soil matrix, whereas there is less influence of soil matrix on the mobile fraction at the same depth. This holds

especially true during the growing season, when the topsoil desiccates and suction cups sample only the immobile fraction. Below 1 m depth, soil water content hardly decreased during the growing season. In contrast, the wetland topsoil was close to saturation even during the growing season. Thus, the effect of preferentially sampling the immobile soil solution fraction due to the use of suction cups was restricted to the upslope top soil, and was the largest in the uppermost soil layer. The effect of sampling with suction cups is less critical at greater depths because of greater mixing of soil solution from different pore sizes at greater depth (Guber et al., 2008; Hohenbrink and Lischeid, 2014; Kamgar et al., 1993).

5.2.4. Quantifying the fraction of variance explained by biogeochemical hot spots

The hot spots identified above are assumed to account for a large fraction of biogeochemical turnover with respect to different biogeochemical processes. This fraction of biogeochemical turnover was estimated using the medians of dimension scores (Table 2). The difference between the minimum and the maximum median of dimension scores of all water sampling groups was assumed to represent 100% of the biogeochemical turnover with respect to the biogeochemical processes. Correspondingly, the difference between the minimum and the maximum median of dimension scores within a hot spot represents a certain fraction of the total turnover in the catchment. For calculating the difference between the minimum and the maximum median of dimension scores within the hot spot in the uppermost 10 cm layer along the wetland flow path median of the topsoil layer (0.03 m depth) along the flow path from upslope soils was used. It was assumed that this value is nearest to the input signal (open field precipitation and throughfall) for both the flow path from upslope soils and the wetland flow path.

Nearly 67% of the variance traced back to redox processes and nearly 53% and 44% traced back to acid induced podzolization could be explained by the hot spots along the flow paths from upslope soils and along the wetland soils, respectively (Table 2). These seem to be plausible numbers, given the role of riparian zones for redox processes and the role of the upper soil layer for podzolization processes. For the hot spots of weathering processes, quantification was not possible because of the effects of preferential sampling of soil solution samples. Given the results for the fractions of the spatial volume of the whole catchment represented by the hot spots (Table 3), these results emphasize the important role of hot spots for biogeochemical turnover in the catchment, which is restricted to a very small part of the spatial volume.

5.3. Streams

Spring and stream sampling sites could not be ascribed to specific positions along a single flow path, as they integrate the contributions of most flow paths. However, different flow paths can contribute in varying degrees to surface water chemistry. Thus, the results of the Isomap analysis help to identify the respective predominant ones.

Scores of all three dimensions at the upslope spring water were in the range of those of soil solution (at 0.9 m depth) and of shallow groundwater (2 m depth). This is in line with the findings of Lischeid and Bittersohl (2008), who found waters from several upslope springs very similar to upslope groundwater from shallow depths. Similarly, waters discharging to the spring were clearly marked by oxic mineralization processes (1st dimension), moderately influenced by acid induced podzolization (2nd dimension) but rather strongly influenced by Al releasing weathering reactions (3rd dimension) as was typical for groundwater from shallow depths outside the wetlands.

The concept of near-surface runoff generation in the wetlands (given by Lischeid and Bittersohl, 2008) is consistent with dimension scores of the Moorbach stream samples which are similar to those of shallow wetland soils. The Isomap results point to strong evidence of anoxic mineralization (1st dimension) and acid induced podzolization processes (2nd dimension), and of Al releasing weathering reactions (3rd dimension).

For the eastern tributary of the Lehstenbach stream near the catchment outlet, scores of all three dimensions were intermediate between deep groundwater and water from the wetland flow paths, as was expected. One third of the catchment area is covered by wetlands. Thus, wetland runoff as well as deep groundwater discharging from upslope soils mix in the Lehstenbach stream (Küsel and Alewell, 2004; Lischeid et al., 2002). In our study, the Lehstenbach stream was sampled mainly during base flow conditions, when mainly groundwater was discharging to the stream (Lischeid et al., 2002). During runoff events, the riparian zones are hydrologically connected to the stream, presumably shifting dimension scores towards those of the wetland samples. In general, the temporal variability in the Lehstenbach stream water chemistry – as well as in the upslope spring water chemistry – likely was underestimated due to the monthly sampling frequency as was demonstrated by Neal et al. (2012).

The results of our study showed that up to 97% of the biogeochemical transformation of the chemical composition of soil solution, groundwater and stream water in the Lehstenbach catchment was restricted to less than 2% of the catchment's regolith, i.e., to the uppermost 0.1 or 0.9 m soil layer. Biogeochemical processes in the deeper aquifer played a negligible role. In addition, processes that were described by the 1st Isomap dimension were restricted to material turnover in wetland soils. For those associated with the 2nd and 3rd Isomap dimension, the uppermost 1 m layer of upslope and wetland soils was equally important. For the 3rd dimension, we found some evidence that preferential sampling of the immobile water fraction in the upslope topsoil blurred clear gradients. Our study considered 15 different solutes and electric conductivity, and found clear evidence of hot spots for all of these solutes.

6. Conclusions

Regarding a catchment as a heterogeneous and multi-species reactor, our study aimed at identifying biogeochemical hot spots along different flow paths in a forested catchment based on numerous soil solution, groundwater and stream water samples. According to the results of the Isomap analysis, about 89% of the total variance could be ascribed to three different bundles of biogeochemical processes that exhibited different patterns along subsurface flow paths. In all cases, the uppermost 1 m layer of the catchment's regolith was identified as a hot spot for the respective biogeochemical processes, although the exact location differed for different process bundles at upslope sites and in wetland soils. It is remarkable that these hot spots constitute the largest fraction of the biogeochemical transformation of all of the investigated 15 solutes. On the other hand, most solutes were affected by more than one of these three process bundles, each of which had different hot spot patterns. As hot spots are often linked to the presence of multiple reactants that depend on the interplay of different biogeochemical processes (McClain et al., 2003; Vidon et al., 2010), it seems to be a promising approach to study hot spots simultaneously for multiple chemical species.

We expect comparable results of the predominating biogeochemical processes for other catchments with similar geology, climate, land use and atmospheric deposition history, leading to comparable water chemistry. Each factor or process influencing the biogeochemical processes in a catchment, like another geology or land use, can change the results of the Isomap analysis. In

general, the Isomap technique is a promising alternative to linear approaches to investigate large multivariate data sets for which non-linearities are expected, independent of the catchment characteristics.

We conclude that an integral approach like that presented in this study would be a useful prerequisite for a biogeochemical modeling approach by reducing the number of processes to the predominating ones ultimately included in the model, focusing on hot spots and including spatial patterns where necessary and appropriate. Thus, the approach can help develop accurate and parsimonious models commonly used for water management purposes.

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Research papers

Stream water quality affected by interacting hydrological and biogeochemical processes in a riparian wetland

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ABSTRACT

Riparian wetlands as both hydrological and biogeochemical hot spots often have a major impact on the release of solutes from headwater catchments. Numerous studies give some evidence of a rather complex interplay of hydrological and biogeochemical processes that is still poorly understood. This study seeks to address this challenge using a multivariate solute concentration data set from a small riparian headwater wetland. First, a non-linear variant of the Principal Component Analysis (Isomap) was performed in a preceding study to identify prevailing biogeochemical processes controlling water chemistry. Second, the scores of the components of the stream draining the wetland were subjected to a cluster analysis to identify typical biogeochemical patterns for different biogeochemical and hydrological boundary conditions.

Four different clusters could be identified, which roughly followed a seasonal pattern, although modified by hydrological boundary conditions in the short-term. During the first three months of the year, Cluster 3 prevailed, indicating a discharge of rather unaltered shallow to mean depth groundwater. Cluster 3 was increasingly replaced by Cluster 2 and then subsequently by Cluster 1, indicating increasingly anoxic conditions, increasing denitrification and desulphurization, and increasing decomposition of organic carbon reflecting increasing biological activity and increasing water residence time within the wetland. However, stream water during stormflow after extended periods of low groundwater level in the second half of the growth season exhibited a very distinct pattern, represented by the fourth cluster. It indicated strong oxic conditions causing enhanced oxidation of sulphides, a corresponding decrease in pH values, and a substantial increase in the concentration of alkaline earth ions, manganese and in electric conductivity during the dry period.

It is concluded that temporal variations in stream water chemistry clearly reflected the intensity of biological activity in the wetland, interacting with water table dynamics. Our results provide strong evidence for major effects of single extreme events like drought periods which are expected to become more frequent because of climate change.

1. Introduction

Riparian wetlands are transition zones between the unsaturated zone, groundwater, and surface water (Casey and Klaine, 2001; Zhao et al., 2009), and are characterized by substantial nutrient and contaminant retention capacities (Fisher and Acreman, 2004). Solute concentration in wetland groundwater and adjacent streams often exhibits remarkable temporal and spatial variance due to varying contributions of soil solution, shallow and deep groundwater, as well as highly heterogeneous patterns of biological and hydrochemical processes within the respective catchment (e.g. Emmett et al., 1994; Kerr et al., 2008; Kull et al., 2008). Processes in the riparian wetlands often superimpose the influence of the hill slope area of the catchment upon surface water quality (Hooper, 2001; O'Brien et al., 2013; Piatek et al., 2009; Prior and Johnes, 2002). A change in biogeochemical processes in the riparian wetlands, e.g. because of increasing intensity and frequency of hydrological extreme events (long dry periods, heavy rainstorms), predicted to become more frequent because of climate change, will thus be likely to affect stream water quality directly (Emmett et al., 1994; Kull et al., 2008; Szkokan-Emilson et al., 2013; Watmough and Orlovskaya, 2015).

The importance of storm events for solute export has been documented in numerous studies (Mitchell et al., 2006; Neal et al., 2006; Raymond and Saiers, 2010; Ulen, 1995). Especially in small

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catchments, a significant amount of annual stream runoff occurs during single runoff events, accompanied by a change of surface water quality within a few hours (Kirchner, 2003).

Systematic shifts of stream water solute concentration during stormflow periods were often ascribed to hydrological processes like changes in water flow paths (Christophersen et al., 1982; Davies et al., 1992; Hagedorn et al., 2000; Lyon et al., 2011). The latter may be due to changes in riparian wetland water table depth, leading to different types of runoff events (Bechtold et al., 2003; Emmett et al., 1994; Inamdar et al., 2008; Kerr et al., 2008). This approach implies that the chemical composition within a single water flow path does not change with regard to time and space, which presumably holds only at the time scale of single stormflow periods. Consequently, the processes causing chemical signatures in runoff are still poorly understood (Aubert et al., 2013b; Dhillon and Inamdar, 2014; Kirchner, 2003).

In contrast to this hydrological perspective, biogeochemists study wetland processes at the time scale of weeks or months, and tend to ignore changing hydrological conditions and boundary fluxes, with the exception of changing groundwater levels. The focus of those studies is on internal processes and not on relating them to output fluxes via the discharging stream (Knorr et al., 2009; Pennington and Watmough, 2015; Reiche et al., 2009). Thus, little is known about the interplay between hydrological and biogeochemical processes in riparian wetlands. So far, various studies have provided anecdotal evidence: Sulphate, e.g., was found to be exported episodically after summer droughts due to oxidation of reduced sulphur (S) compounds (Eimers et al., 2007; Inamdar et al., 2008; Tipping et al., 2003; Zhang et al., 2010). The modelling study by Frei et al. (2012) illustrated how small scale spatial heterogeneity of flow paths and biogeochemical processes could yield a complex pattern of stream solute concentration during stormflow.

Various studies elucidated the interplay between hydrological and biogeochemical processes affecting solute export from riparian wetlands (Arnold et al., 2015; Piatek et al., 2009; Vidon et al., 2014), including fluctuating climatic conditions (Kull et al., 2008), seasonal factors (Muller and Tankéré-Muller, 2012) including seasonal hydrologic events (Kerr et al., 2008), changes in the water flow pathways (Christophersen et al., 1982; Kerr et al., 2008; Mitchell et al., 2006), antecedent moisture conditions (Inamdar et al., 2009; Mitchell et al., 2006), redox processes (Kerr et al., 2008), available solute concentration in the wetland (Piatek et al., 2009), dilution of solutes (Inamdar et al., 2009), and the flushing of solutes after drought periods (Emmett et al., 1994; Szkokan-Emilson et al., 2013). Aubert et al. (2013b) investigated seasonal patterns of flood-induced variability in stream water chemistry by using a probabilistic clustering method. Inamdar et al. (2013) highlighted the need to recognize temporal shifts in the end-member chemistry as a function of catchment wetness to better characterize catchment flow paths and mixing responses. Knorr (2012) emphasized the importance of both hydrological and redox conditions in the wetlands for solute export in the catchment of this study.

Water resources management must consider spatial and temporal patterns of biogeochemical and hydrological processes for assessing the impact of climate and land use change on solute export. Management practices are often based on results from biogeochemical modelling. However, non-linear interactions between hydrological and biogeochemical processes in catchments render the understanding and prediction of long-term behaviour of surface water quality difficult. Thus, the objective of this study was to elucidate the interplay between biogeochemical and hydrological processes and to weight their respective relevance with regard to water quality in the receiving stream. It was hypothesized that the temporal patterns of wetland stream water chemistry were not related to changes in hydrological flow paths but that stream water chemistry reflected varying antecedent biogeochemical boundary conditions in the wetland. However, it was assumed that biogeochemical processes in the wetland were affected by the groundwater level which determined the degree of anoxia in the uppermost soil layer.

This study builds upon a preceding study by Weyer et al. (2014). Prevailing biogeochemical processes in the Lehstenbach catchment were identified in a comprehensive data set comprising soil solution, groundwater, spring water, and stream water solute concentration data from upslope and wetland sites using the Isomap approach (Isometric Feature Mapping; Tenenbaum et al., 2000). Isomap can be considered a non-linear variant of Principal Component Analysis (PCA). As different observables of the multivariate water quality data set exhibited numerous, although partly non-linear relationships, a large fraction of the variance could be represented by a small number of Isomap components. As these components were independent, they were used to identify the prevailing biogeochemical processes. In addition, the component scores were used as a proxy for quantifying the intensities of the respective biogeochemical processes.

This study focused on a subset of the data set used by Weyer et al. (2014), comprising data from 280 samples taken in a stream that drained a small wetland in the Lehstenbach catchment. In addition to solute concentration values, the Isomap component scores of the samples as a quantitative assessment of the intensity of the prevailing processes were included. This study aims at a better understanding of the observed pronounced temporal variability of stream water quality, i.e., at differentiating between biogeochemical and hydrological drivers. To that end, a Cluster Analysis (CA) was used to classify stream water samples. As that classification was based on the scores of the independent Isomap components, it does not only solve the problem of collinearity as is often recommended (Fröhlich et al., 2008; Menció and Mas-Pla, 2008; Woocay and Walton, 2008). Moreover, it allowed interpreting the clusters in terms of intensities of identified biogeochemical processes which would not be possible by using solute concentration data. A time series of cluster assignment of the stream water samples was related to the respective meteorological and hydrological boundary conditions, and conclusions were drawn with respect to the interplay between biogeochemical and hydrological processes. In addition, the classification of stream water samples was compared to the well-known Schöller- and Piper-classification of water samples (Piper, 1944; Schoeller, 1962). Finally, implications for explaining temporal patterns of single solutes in stream water quality are discussed.

2. Data and methods

2.1. Data

The current investigation involved samples of a wetland stream within the Lehstenbach watershed (50°08′N and 11°52′E) in the Fichtelgebirge Mountains in southeast Germany. Extensive monitoring programs have been run in this catchment since the end of the 1980s, including several studies on groundwater and stream water chemistry.

The watershed area is 4.19 km^2 and elevation ranges from 690 to 877 m a.s.l. (Fig. 1). The bedrock consists of variscan granite of two different facies (Stettner, 1964), which show very similar mineralogical compositions. Significant differences between the two facies with respect to geochemistry (Weyer et al., 2008) or hydrogeology (Partington et al., 2013) have not been observed. The thickness of the regolith is up to 40 m and more. Dystric cambisols and podzols predominate. In the riparian zone, fibric histosols and dystric gleysols are present, representing about one-third of the watershed area. The area is drained by a dense network of natural streams and artificial channels. Dense Norway spruce stands (*Picea abies*) cover more than 95% of the watershed area. Annual mean air temperature is 5.8 °C, annual mean precipitation is between 950 and 1250 mm. Annual mean runoff of the Lehstenbach stream, i.e. the catchment outlet, was 470 mm during the period from 1991 to 2001 (Lischeid et al., 2010). Snowpack usually develops in December or January, and final snowmelt occurs in March or April. The site has been severely impacted by sulphate deposition that peaked in the 1970s and has decreased by more than 80% since

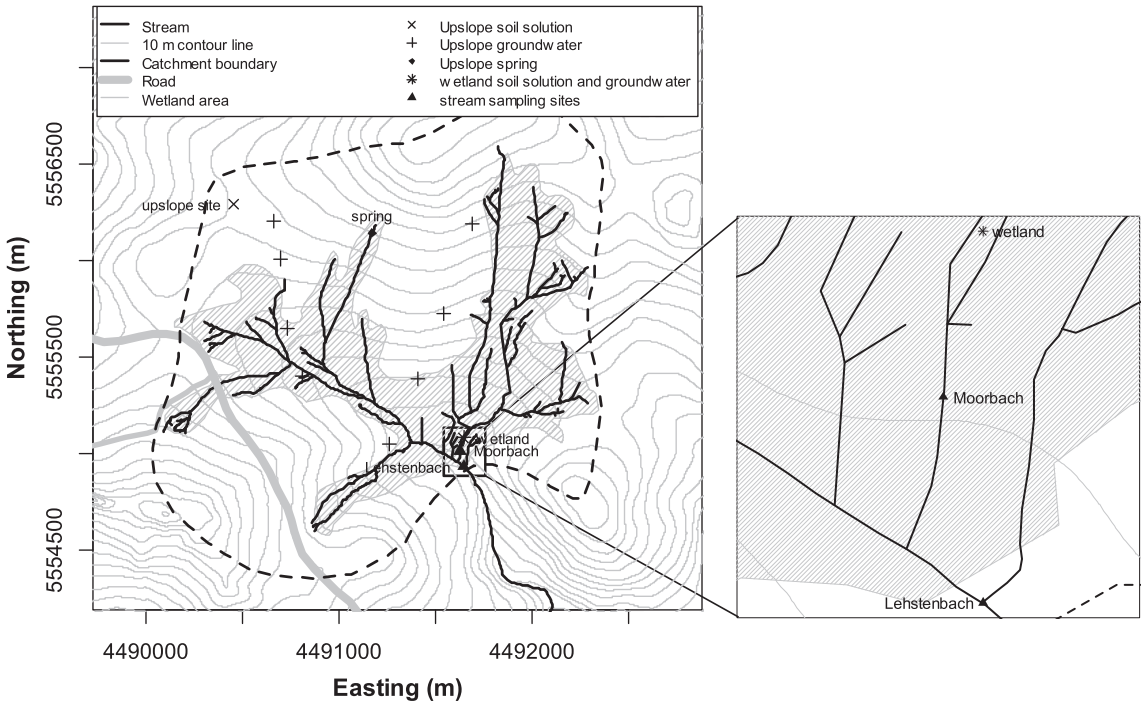

Fig. 1. Map of the Lehstenbach watershed. Gauss-Krüger coordinates [m] are given at the axes. Moorbach: Moorbach stream; Lehstenbach: Lehstenbach stream.

then (Matzner et al., 2004).

This study focused on the ephemeral Moorbach stream that drains the slightly acidic Schlöppnerbrunnen fen, later referred to as "wetland", near the catchment outlet (Fig. 1). The fen area is 0.08 km^2. The thickness of the peat layer on top of the mineral soil ranges between 30 and 70 cm (Reiche et al., 2009). The runoff of the Moorbach stream is exclusively composed of wetland waters, i.e. by waters that originate in the wetland or by groundwater that has passed through the wetland area. Discharge of the Moorbach stream was between 0 and 4 l/s during most of the study period. During discharge peaks, up to 439 l/s were observed. Three plots of 7.2 m × 5 m each were subjected to two drying/rewetting experiments from August to September 2006, and from May to July 2007 (for more details see Reiche et al., 2009). The rest of the wetland was not manipulated.

More than 600 stream water samples from the Moorbach stream were taken between April 2005 and November 2007 with an ISCO automatic sampler at daily intervals. No samples could be taken during the frost period or when the Moorbach stream fell dry. Samples were filled in thoroughly-rinsed polyethylene bottles in the automatic sampler. The filled bottles were at least collected every three weeks and directly transported to the central laboratory of the Bayreuth Center of Ecology and Ecological Research (BayCEER). In all collected samples, electric conductivity (EC) and pH values were measured directly after collection with a TetraCon® 325 conductivity cell (WTW), and with a SenTix® 41–3 electrode (WTW), respectively.

Initially, from April to June 2005, daily stream water samples were analysed. Afterwards, only samples taken during runoff events were selected according to stream discharge and electric conductivity values. In total, 280 stream water samples were selected to be analysed as described below.

Selected water samples were filtered through a cellulose-acetate-membrane filter with 0.45 µm pore size. They were stored in thoroughly-rinsed polyethylene bottles in the dark at 2 °C until further analysis. The element concentrations of aluminium (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), total sulphur (S) and silica (Si) were analysed by ICP-OES (Varian Vista-Pro CCD Simultaneous). Chloride (Cl), nitrate (NO_3) and sulphate (SO_4) were analyzed using ion chromatography (IC Dionex DX 500), dissolved organic carbon (DOC) by temperature combustion and subsequent determination of carbon dioxide (CO_2) (Analytik Jena Multi N/C 2100F), and ammonium (NH_4) by Flow Injection Analysis (FIA-LAB by MLE). Quality assurance of the data was performed prior to this study by the central laboratory of the Bayreuth Center of Ecology and Ecological Research (BayCEER).

2.2. Methods

Data handling, statistical analysis and plotting were performed using the R environment (R Development Core Team, 2006). The Cluster Analysis was performed with the package "cluster" (Maechler et al., 2007). The packages "Hmisc" (Harrell et al., 2014), "multcompView" (Graves et al., 2012) and "hydrogeo" (English, 2017) were used to produce the graphics.

2.2.1. Statistical analysis

Different (non-linear) multivariate statistical methods were used sequentially to analyse water solution data. A global flowchart of the different steps of statistical analysis is shown in Fig. 2.

2.2.1.1. Preceding analysis of water quality data. The data set used for this study is a subset of the original data set used by Weyer et al. (2014), comprising soil solution, groundwater, spring water and stream water samples from various sites within the catchment, including upslope soils.

Weyer et al. (2014) applied a non-linear version of a Principal Component Analysis, the Isometric Feature Mapping (Isomap) approach, to the original data set in order to identify the prevailing biogeochemical hot spots along different subsurface flow paths from the soil surface to the catchment outlet. The approach reduced the dimensionality of the original data set, comprising 1686 single samples with 16 parameters each, down to three components (Fig. 2). The three components explained 89% of the total variance (48%, 30%, and 11%, respectively). The first component was positively correlated with SO_4, NO_3, Mn, K, Mg and Ca concentrations and electric conductivity, but was negatively correlated with Fe and Si concentrations and pH values. The second component was associated with high DOC, Fe, and Al

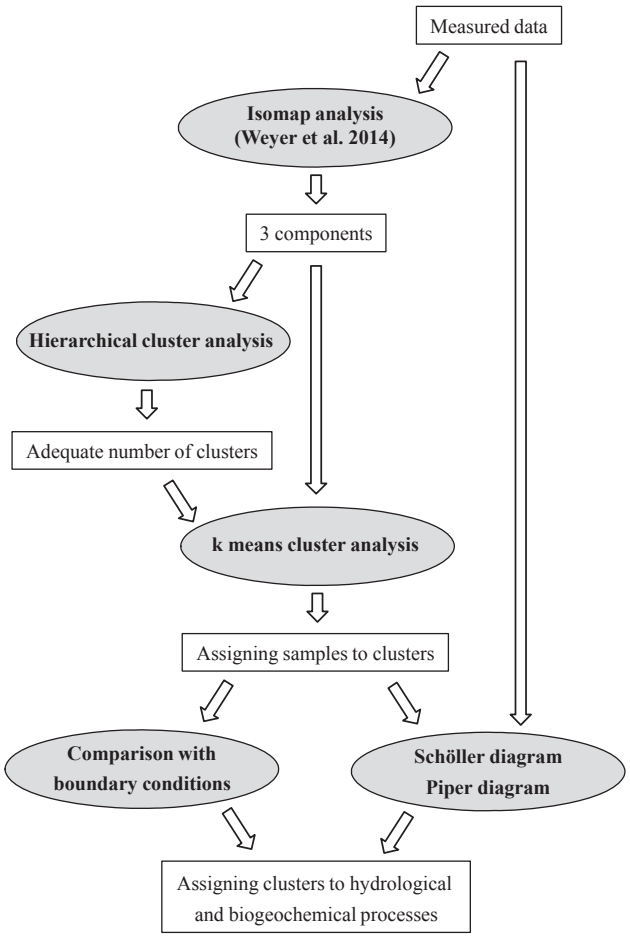

Fig. 2. Flowchart of the approach followed using different methods (grey shaded ellipses).

concentrations, but low SO_4 and Na concentrations and low pH values. The third component was characterized by positive loadings of Cl, Si, NH_4, K, Na, and pH values and negative loadings of Al, and SO_4. The first component was ascribed to redox processes, the second to acid-induced podsolization, and the third to weathering processes in the subsurface (Weyer et al., 2014). Every sample of the data set was assigned a score of the respective components as a quantitative measure for the strength of the respective effects on that water sample. It could be shown, that for all three components the uppermost 10 cm of the riparian wetland as well as the uppermost 1 m of upslope soils played a crucial role for solute concentration in the receiving streams.

For this study, a subset of data from a small wetland stream was used as described above. It was assumed that the three biogeochemical processes identified with the Isomap approach prevailed in the whole catchment, including the wetland site. Thus, the Cluster Analysis was performed on the scores of the first three components of the Moorbach stream samples rather than on the values of the 16 solutes. This was done as it was recommended to perform a Cluster Analysis on whitened data in order to not give too much weight to parameters that were strongly correlated to each other. On the other hand, the original data set used by Weyer et al. (2014) contained chemical information from various water sources, including soil solution and groundwater from upslope and wetland sites. It was therefore expected, that it would reflect, to a larger degree, processes that are more visible in other parts of the catchment, like acid-induced podsolization. In addition, results of this study can be directly related to that of the Weyer et al. (2014) study.

2.2.1.2. Cluster Analysis (CA). A Cluster Analysis was performed using the scores of the first three Isomap components of 280 Moorbach stream water samples selected from the original data set used by Weyer et al. (2014) in order to group water samples that were influenced by the same biogeochemical processes (Fig. 2). Cluster Analysis aims at classifying samples according to a similarity measure and a grouping algorithm. Agglomerative hierarchical cluster analysis uses the distance between samples as a measure of similarity (Vega et al., 1998). At different distances, different clusters will form, which can be represented using a dendrogram. In contrast, the k-means clustering aims at finding the cluster centroids for a given number of clusters. Objects are assigned to the nearest cluster centroid by minimizing the squared distances from the latter.

The Isomap scores of the Moorbach stream water samples were first normalized to zero mean and unit variance for each component separately. First, a hierarchical clustering (agglomerative nesting) was performed (Fig. 2) to assess an adequate number of clusters using the knee criterion (Dubes and Jain, 1979; Tibshirani et al., 2001), i.e., a compromise between a minimum number of clusters and a minimum sum of squared errors of assignment to clusters. The sum of squared errors is defined as the sum of the squared distance between each member of a cluster and its cluster centroid. Using the number of clusters found in this manner, in a second step, a k-means clustering was performed (Fig. 2). The centroids of each cluster and the distances between the observations and the cluster centroids were calculated. Observations with a smaller distance to another centroid than to the own centroid were then relocated to the other cluster in an iterative procedure.

The Cluster Analysis yielded a classification of the 280 water samples. In a next step, the clusters were analysed for significant differences with respect to component scores as well as to solute concentration. To that end, the Wilcoxon test with Bonferroni correction for multiple testing was used for pairwise comparison between different clusters. In contrast to, e.g., the well-known *t*-test, the applied test can handle strongly differing numbers of samples per group and does not require any specific distribution. Level of significance was 5% in all cases.

The same test was used to test for significant differences between the clusters with respect to the boundary conditions of the sampling dates. Boundary conditions were characterized by daily mean values of discharge, groundwater level, precipitation, air temperature and Julian day of the sampling dates. Discharge was logarithmised after adding a constant offset of 1 l/s in order to avoid logarithmising of zero values. Precipitation was summed up for a period of 30 days before each sampling date, respectively. In addition, a rough proxy for water residence time in the riparian wetland was used by determining the number of preceding days since the last exceedance of a discharge threshold of 1 l/s. Determination of that proxy variable was possible only for periods without data missing from the hydrograph. Thus, part of the water samples could not be assigned a value of that proxy variable.

For visualization of differences between clusters, box-percentile plots were used. They can be regarded as approximations of the probability density of the respective variable, but rotated by 90°. More precisely, the width of the figure is proportional to the percentile of that height up to the 50th percentile. Above the 50th percentile, the width is proportional to 100% minus the percentile. Thus, the width at any given height is proportional to the percent of observations that are more extreme in that direction. In addition, the first, second, and third quartile is marked by horizontal lines (Esty and Banfield, 2003).

2.2.2. Schöller and Piper classification of stream water samples

To allow for comparison with standard methods of multivariate water quality visualisation, stream water quality and cluster means were plotted in Schöller and Piper diagrams (Fig. 2). For the Schöller diagram, mean values, the 10th and the 90th percentiles of solute concentration of the stream water samples were plotted for each of the four clusters. For the Piper diagram, charge equivalents of Ca, Mg, Na,

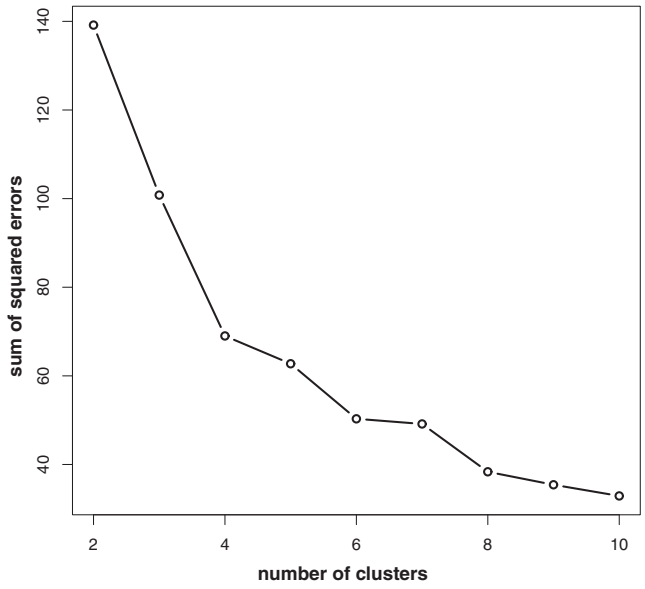

Fig. 3. Sum of squared error of cluster assignment vs the number of clusters for the last ten steps of the agglomerative cluster analysis.

K, Cl, NO_3, SO_4 and hydrogencarbonate and bicarbonate (HCO_3^- and CO_3^{2-}) were calculated. Then, the percentage of each cation and anion with respect to the total sum of cations and anions, respectively, was calculated. Stream water samples assigned to the same cluster were plotted using the same symbol in order to differentiate between the four clusters.

3. Results

3.1. Identification of clusters

The appropriate number of clusters was chosen using the sum of squared errors within a group plotted against the number of clusters (Fig. 3): at the point where the reduction of sum of squared errors with increasing number of clusters slowed down markedly. This point was found at four clusters, subsequently named Cluster 1 to Cluster 4. Each of the 280 water samples was assigned to one of these four clusters: 56 samples to Cluster 1, 101 to Cluster 2, and 93 and 30 to Cluster 3 and 4, respectively.

Fig. 4 gives the scores of the first three Isomap components, Fig. 5 shows the pH values, electric conductivity and concentration of selected solutes for each of the four clusters. Different letters a, b, c, and d denote the significantly different median values of the respective Isomap component scores and the respective variables between the respective clusters in Figs. 4 and 5, respectively. All clusters differed significantly with respect to the scores of all three components, and for most of the solutes as well, except for NH_4 (not shown). Scores of the first component increased systematically from Cluster 1 to 4, indicating increasingly oxic conditions. In contrast, scores of the second component decreased systematically, pointing to decreasing acid-induced podsolization. A different pattern was exhibited by the scores of the third component. Scores increased from Cluster 1 to 3 and decreased for Cluster 4 again (Fig. 4). Peak values for the third cluster indicated the strongest effect of weathering processes for these samples, which was typical for groundwater at greater depths (Weyer et al., 2014).

These patterns were reflected by three different groups of solutes. The first group, comprising of electric conductivity, SO_4, Ca, Mg, Mn and S (not shown) exhibited an increase from Cluster 1 to 4, similar to the scores of the first component. The opposite was true for the second group, including pH, DOC, Al and Fe, similar to the scores of the second component. The pattern of the third component was mimicked by the third group, i.e., by Si, K and NO_3. The same held for Na and Cl (not shown).

3.2. Time series and typical boundary conditions

Time series of cluster assignment of the 280 stream water samples during the 2005–2007 sampling period are shown in Fig. 6 and were compared to that of discharge and groundwater levels in the riparian wetland. In addition, Julian day and the respective meteorological and hydrological boundary conditions during sampling days are compared to cluster assignments in Fig. 7.

On average, samples were taken every 3–4 days. However, sampling intervals differed widely between one hour and 99 days, partly due to the stream occasionally drying up. In general, assignment to clusters exhibited considerable persistency: in more than 80% of all cases, consecutive samples were assigned to the same cluster. A systematic change of cluster occurrence before, during or after runoff events could not be observed. Thus, pronounced changes of stream water solute concentration could be ascribed, in the first place, to slowly modifying conditions within the wetland rather than to short-term hydrological processes.

Time series of assignment to clusters roughly followed a seasonal pattern, although with considerable modification within and between the years. Samples taken during the first three months of the year were exclusively ascribed to Cluster 3 (Figs. 6 and 7). Correspondingly, air temperature during sampling was the lowest, groundwater level the highest, and time since last preceding discharge peak (as a rough proxy for water residence time within the wetland) the shortest compared to all clusters (Fig. 7).

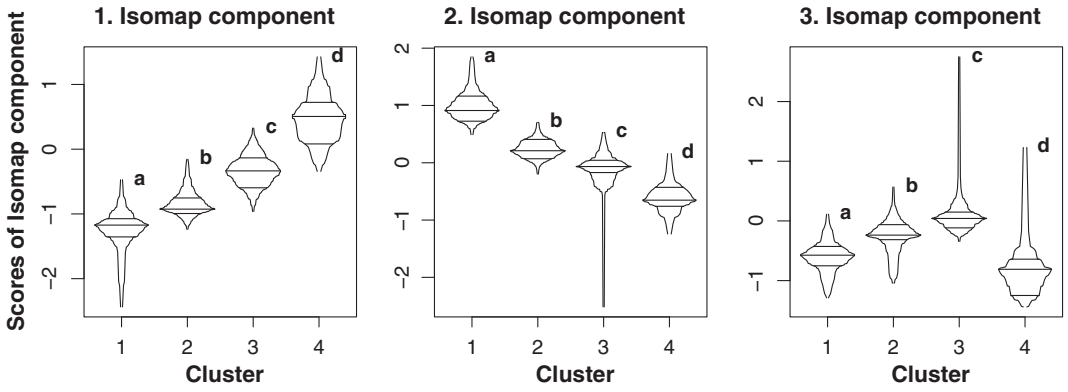

Fig. 4. Box-percentile plots of the scores of the first three Isomap components (1st, 2nd, 3rd) for each of the four clusters. The width at any given height is proportional to the percent of observations that are more extreme in that direction (Esty and Banfield, 2003). Horizontal lines mark the median, 25th and 75th percentiles. Significant differences between the clusters are denoted by different letters a, b, c and d.

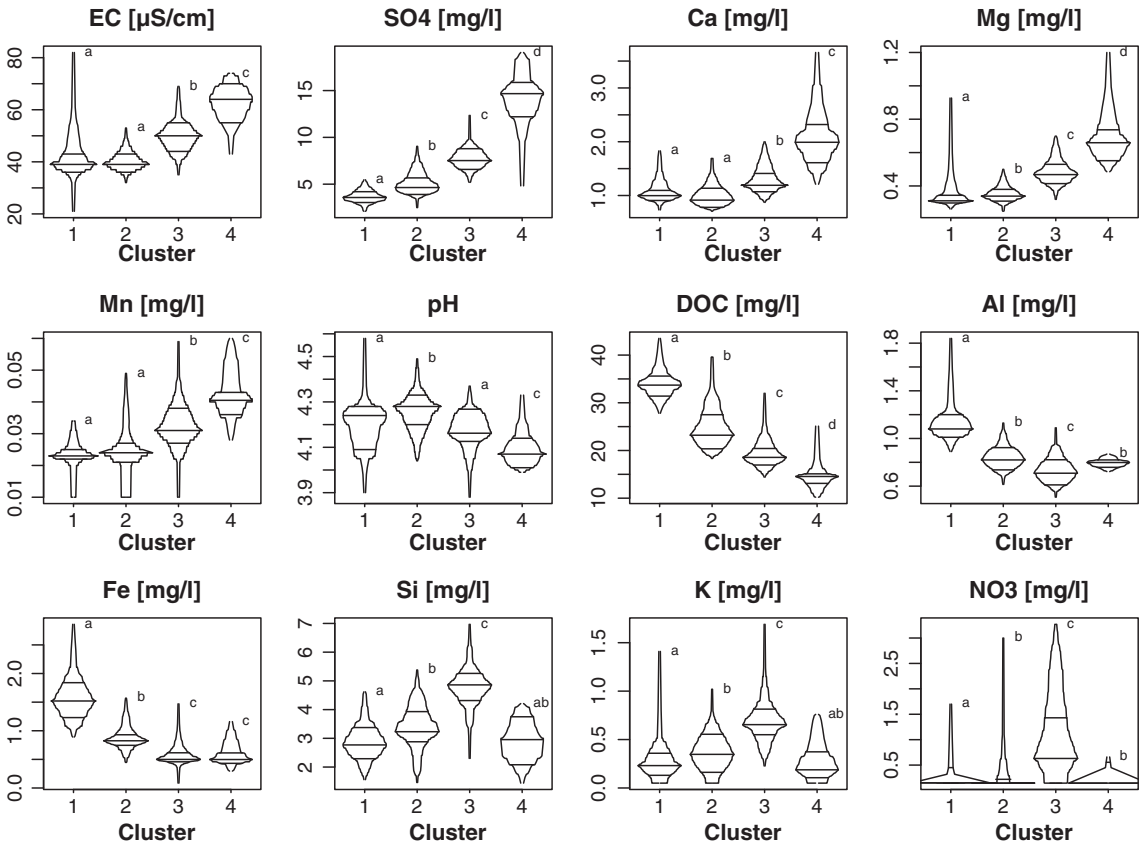

Fig. 5. Box-percentile plots of the concentration of different solutes, electric conductivity (EC) and pH-values for each of the four clusters. Significant different distributions of the respective variables between the respective clusters are denoted using different letters a, b, c and d.

Later in the year, Cluster 3 was subsequently replaced by Cluster 2, and then by Cluster 1 (Fig. 6), along with rising air temperature and lower groundwater level (Fig. 7). Likewise, cumulative precipitation for a 30 day-period was the lowest for Cluster 2. Correspondingly, scores of the first component decreased, indicating increasingly anoxic conditions. Groundwater level and cumulative precipitation for Cluster 1 was significantly higher than for Cluster 2, representing recovering of the groundwater level after periods of moderate groundwater level drawdown (less than 15 cm). Increasing scores of the second component pointed to increasing effects of acid-induced podsolization, and decreasing scores of the third component to decreasing effects of weathering processes. Thus, stream water became increasingly dissimilar compared to groundwater solute concentration.

Four samples in early July 2005, and another 26 samples in 2006, mostly in August and October, were assigned to Cluster 4 (Fig. 6). During all of these three periods, groundwater level was low (Fig. 7), but recovered from preceding extensive drawdown (Fig. 6). Correspondingly, water residence time within the riparian wetland was on average the largest for Cluster 4 (Fig. 7). Cumulative precipitation was intermediate. In contrast to 2005 and 2006, there was no similar drawdown of groundwater level after mid-May in summer 2007, and no sample was assigned to Cluster 4 (Fig. 6).

Although samples of Cluster 4 usually followed immediately after those of Cluster 1 or 2 (Fig. 6), they differed to a maximum extent with respect to scores of components 1 and 2 (Fig. 4), and with respect to most solutes (Fig. 5). Scores of the first and of the second component of Cluster 4, compared to those of Cluster 1 (Fig. 4), indicate that this change came along with a drastic reoxidation and a strong decrease of acid-induced podsolization. Depending on the respective hydrological conditions, Cluster 4 was then either rapidly replaced by Cluster 1 (2005) or by Cluster 2 or 3 (2006) (Fig. 6).

Cluster occurrence did not vary between base flow and storm flow conditions as long as the water table was near the soil surface (runoff events April and May 2005, January 2007; Fig. 6). Furthermore, there seemed to be no dependence of cluster occurrence on the magnitude of the runoff event. For example, discharge of the Moorbach stream after two comparable periods of extensive groundwater level drawdown (more than 20 cm) was 1.76 l s^{-1} and 20.22 l s^{-1} in July 2005 and October 2006, respectively, with a comparable cluster occurrence. Similarly, discharge of the Moorbach stream after three periods of moderate groundwater level drawdown (less than 15 cm) was near 0 l s^{-1}, 43.10 l s^{-1} and 12.84 l s^{-1} in June 2005, June 2007 and August 2007, respectively, also with a comparable cluster occurrence. Correspondingly, there was no significant difference between average discharge values for Cluster 1 and 4 (Fig. 7), the most differing clusters with respect to water chemistry (Figs. 4 and 5).

The two drying/rewetting-experiments conducted from August to September 2006 and from May to July 2007 in three of the six sampling plots in the wetland under study did not seem to have an influence on stream water quality. Indeed, cluster occurrence in the Moorbach stream water samples taken during and after the experiments could be explained by naturally occurring hydrological conditions.

3.3. Schöller and Piper classification of cluster means and stream water samples

All of the four clusters showed comparable patterns in the Schöller diagram (Fig. 8). Highest mean concentrations were observed for SO_4, followed by Si and Na. Lowest mean concentrations were observed for Mn and NH_4. Mean solute concentrations differed for the different clusters with respect to Ca, Mg, Fe, NO_3, SO_4 and DOC. Corresponding to the results of the CA, Cluster 4 showed the highest mean SO_4 concentration.

Using the Piper diagram (Fig. 9), stream water samples can be

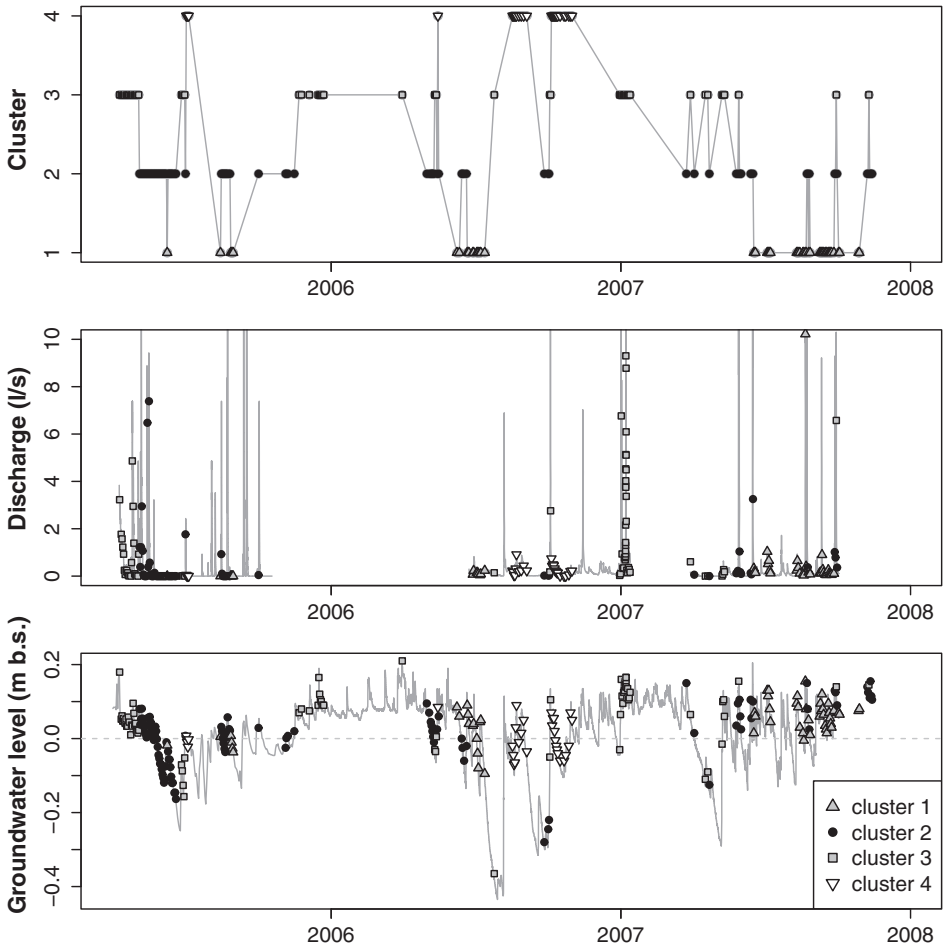

Fig. 6. Time-series of assignment of water samples to the four clusters, discharge of the Moorbach stream, and groundwater level below surface in the wetland.

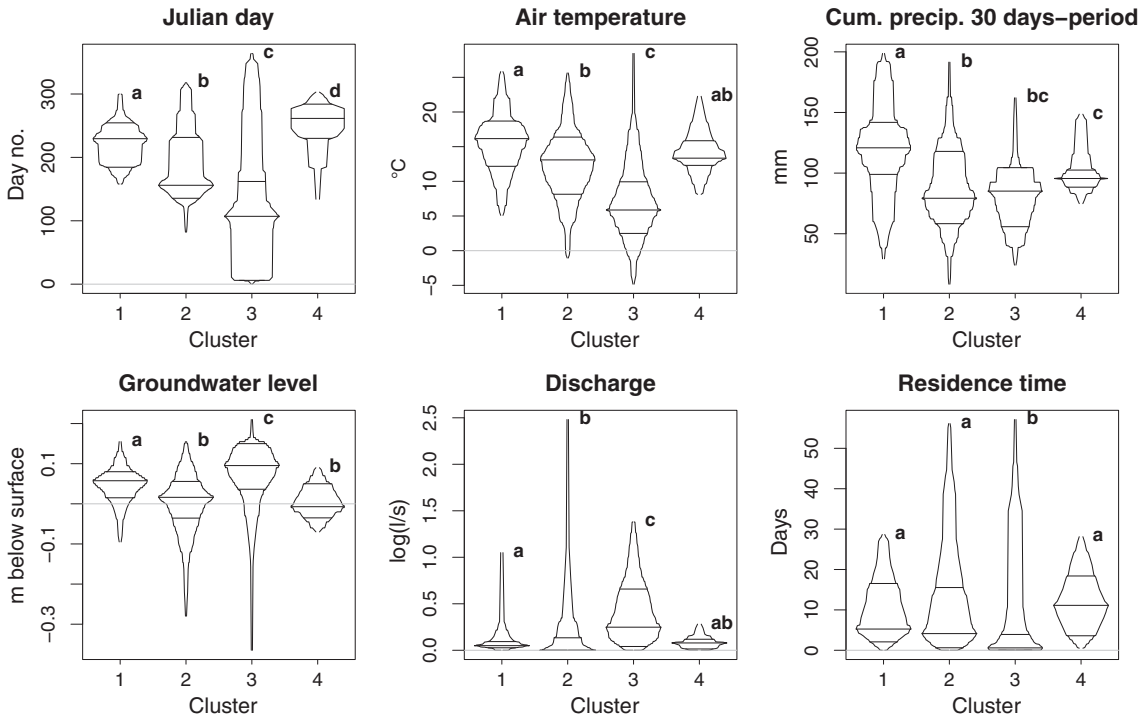

Fig. 7. Box-percentile plots of candidate predictor variables for each of the four clusters in order to characterize the boundary conditions of the sampling dates. Significant differences between the respective clusters are denoted by different letters a, b, c and d.

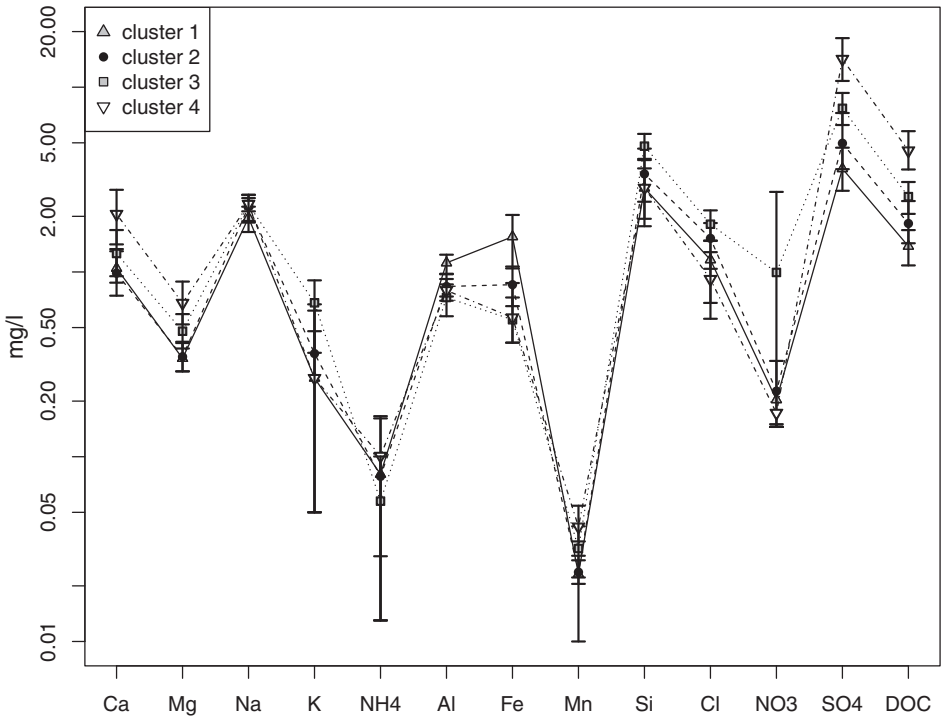

Fig. 8. Schöller diagram of mean concentrations (mg/l) of the wetland stream water samples assigned to the four clusters. Lower and upper limit of the error bars represent the 10th and the 90th percentiles.

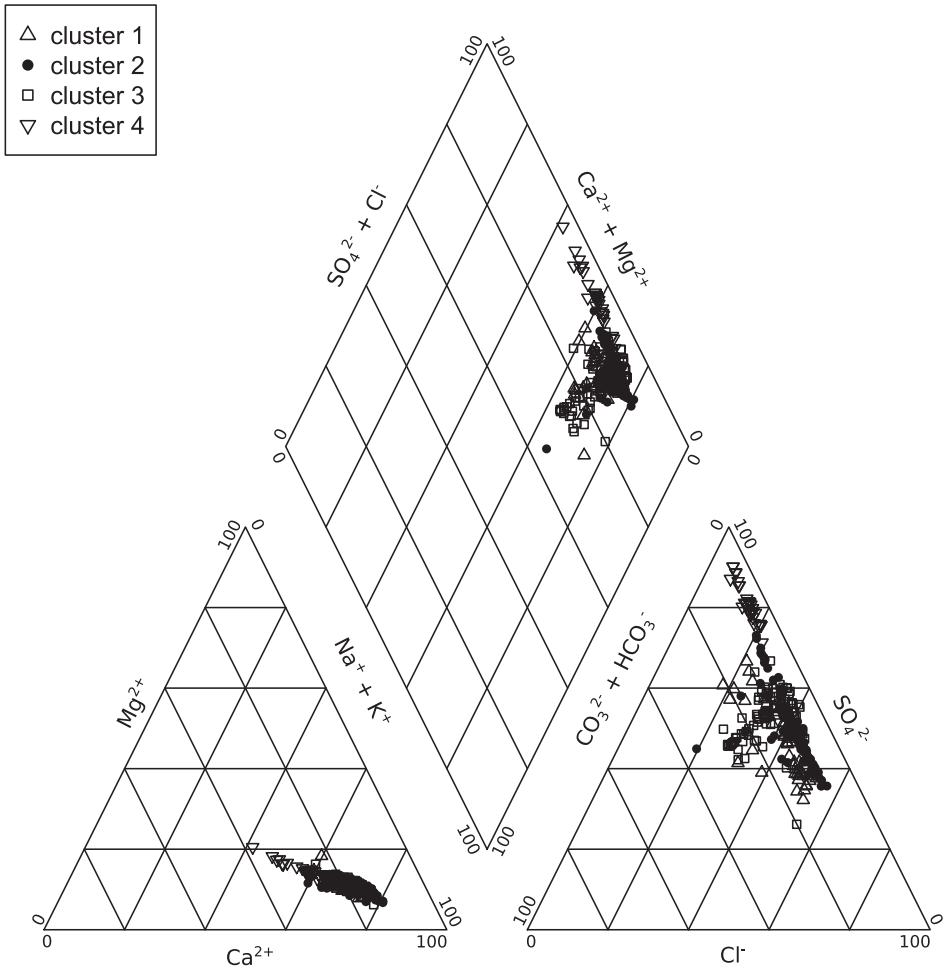

Fig. 9. Piper diagram of the 280 wetland stream water samples assigned to the four clusters.

classified as sodium-potassium type and as chloride to sulfate type. Water samples assigned to Cluster 4 showed considerably higher SO_4 and Ca, but lower Cl concentrations than water samples assigned to the other clusters. In contrast, water samples assigned to Cluster 3 showed remarkably lower SO_4 concentrations but higher $CO_3^{2-} + HCO_3^-$ concentrations. Water samples assigned to Cluster 1 showed the lowest SO_4 concentrations but higher Cl concentrations compared to the other water samples.

4. Discussion

This study aimed at elucidating the interplay between internal biogeochemical processes in a riparian wetland and hydrological processes at the time scale of days to months. The samples are regarded as representative samples of the wetland water being mobilized especially during single runoff peaks. Clustering necessarily implies ignoring within-cluster variability and overemphasizing differences between clusters. Although the knee criterion, applied here for selection of an adequate number of clusters, is widely accepted (Dubes and Jain, 1979; Tibshirani et al., 2001), any clustering of a presumably more or less continuous data set is, to a certain degree, arbitrary. Consequently, assignment of single samples to certain clusters can always be questioned. However, clustering can help identify certain structures in large data sets.

In this study, samples were clustered based on the scores of an Isomap analysis that determined the independent components. Each of these components had been interpreted as a quantitative measure of the strength of the effect of single processes in a preceding study (Weyer et al., 2014). However, this interpretation is not a necessary prerequisite for this study and the inferences drawn from the results. As has been illustrated in Fig. 5 clusters can be equally well analyzed and interpreted in terms of solute concentration. Different clusters can be distinguished in the Piper and the Schöller diagrams as well (Figs. 8 and 9), although observable differences between clusters in the two diagrams were less clear compared to the classification by the CA. However, in general, results of the Piper and Schöller classification were in line with the results of the CA. For example, Clusters 1, 3 and 4 could be distinguished in the Piper diagram, mainly with respect to Ca and SO_4 (Fig. 9).

The sampled stream had its only source in the wetland. The wetland is a discharge area of groundwater that had been recharged further uphill (Partington et al., 2013). This groundwater is characterized by very low scores of the second Isomap component, that is, low acid-induced podsolization, and high scores of the third component, indicating strong effects of weathering (Lischeid and Bittersohl, 2008; Weyer et al., 2014). Temporal variability of these effects is very low. Thus, taking groundwater solute concentration as a background, any modification observed in the wetland stream has to be ascribed to wetland internal processes. The stream was sampled roughly 50 m downstream from its source. Thus, in-stream processes do not need to be accounted for, due to a very short residence time within the stream.

In the following, the four different clusters are first discussed, emphasizing the interplay between the typical biogeochemical processes represented by the clusters with the different hydrological and seasonal boundary conditions, respectively. Corresponding to the results section, clusters are discussed in chronological order of occurrence during the course of the year. Then, implications for the temporal variability of stream water chemistry during runoff events and for the temporal patterns of single solutes in the Moorbach stream water are discussed.

4.1. Cluster 3: Discharging unaltered groundwater

In winter and early spring, when the temperatures and the microbial activity are low, only Cluster 3 was observed (Fig. 6). Anoxic redox processes (first component) seemed to play a minor role, reflected by low negative mean component scores, although the wetland is completely water saturated due to low evapotranspiration. Obviously, microbial oxygen consumption and subsequent reduction of the redox potential in the wetland was very low in winter and early spring due to low temperatures and did hardly alter the quality of the groundwater discharging into the wetland stream. In addition, residence time of water within the wetland was the shortest for samples of Cluster 3 (Fig. 7), which adds to the effect of slow kinetics of biogeochemical processes during the winter months. Correspondingly, the highest NO_3 and relatively high SO_4 and DOC values were observed in the Schöller diagram (Fig. 8).

4.2. Clusters 2 and 1: Enhanced microbial activity and anoxic conditions

Cluster 2 ranges between Cluster 3 and 1 with respect to all Isomap components and to all solutes (Figs. 4 and 5). In the Piper diagram as well, Cluster 2 is placed between Cluster 3 and Cluster 1 (Fig. 9). Cluster 2 is considered a transitional stage between the two. This holds for the temporal order of cluster occurrence as well, although with some minor exceptions (Fig. 6). Thus, both clusters are discussed in a common section.

Simultaneously with rising temperatures in spring and early summer, Cluster 3 was subsequently replaced by Clusters 2 and 1 in every year of the study period (Figs. 6 and 7). Rising air and soil temperature likely led to a considerable increase of microbial activity, and thus to more rapid kinetics of the respective processes. On the other hand, increasing transpiration lowered the groundwater level in the wetland, and thus decreased the frequency of runoff peaks. The data of another riparian wetland in the Lehstenbach catchment presented by Frei et al. (2010) illustrated the relationship between groundwater level and discharge. Decreasing frequency of runoff events in turn resulted in increased mean residence time of water within the wetland (Figs. 6 and 7). Thus, the effects of microbial activity became even more pronounced. Consequently, oxygen depletion set in, and the scores of the first Isomap component decreased, indicating increasingly anoxic conditions, as was observed in other studies as well (Kull et al., 2008; Olivie-Lauquet et al., 2001). Please note that scores of that component reflect conditions in the wetland, rather than conditions in the wetland stream, which in fact was oxic due to being exposed to the atmosphere. Instead, very low NO_3 and SO_4 concentrations in stream water samples (Fig. 5) were indicative of denitrification and desulphurication in the wetland. Anaerobic mineralization could be stimulated by regeneration of electron acceptors due to frequent fluctuations in the water table, and thus drought and rewetting events (Blodau and Moore, 2003; Deppe et al., 2010; Knorr et al., 2008; Knorr et al., 2009). Such fluctuations were observed within the uppermost 15 cm in the wetland of the study site during the period of August to September 2007, when most of the samples were ascribed to Cluster 1. Correspondingly, on average, the highest cumulative precipitation for a 30 day-period as well as a higher groundwater level for Cluster 1 compared to Cluster 2 was observed. Because SO_4 was by far the dominating anion, concentration of alkaline earth cations and of Mn in the stream decreased as well (Fig. 5). Contrary to common expectations, Mn concentration in the Lehstenbach catchment is obviously more closely related to ionic strength rather than to redox processes (Lischeid and Bittersohl, 2008). Similarly, increasing Mn concentration with increasing redox potential was observed by Frohne et al. (2011) in soils instead of the expected precipitation of Mn oxides, presumably due to an equally low pH, as in this study, and to precipitation of Mn sulphides. Increasing residence time increased the effect of other biogeochemical processes in the wetland as well. These processes are not necessarily related to temperature. Clusters 2 and 1 exhibited enhanced effects of acid-induced podsolization processes (higher mean scores of the second component) and Al-releasing weathering reactions (lower mean scores of the third component) discharging to the Moorbach stream when compared to Cluster 3. Similar observations were found by Olivie-Lauquet et al. (2001). They suggest that the microorganisms which use soil iron and

manganese oxy-hydroxides as electron acceptors catalyzed the change of redox conditions and induced an increase of DOC concentration. The close relationship between Fe-reducing conditions and DOC release corresponds to the findings of Knorr (2012) at the wetland site of our study and with the results of Lambert et al. (2013). Concomitantly, trace elements like Al adsorbed to the Fe(hydr)oxides are released (Stumm and Sulzberger, 1992; Trolard et al., 1995). These processes likely produce a chemical composition of water samples similar to that produced by acid-induced podsolization processes associated with the second component and likely add to the latter. In addition, the enhanced podsolization processes in the wetland compared to Cluster 3 could be explained by aeration of the top of the small hummocks in the wetland (cf. Frei et al., 2010). In fact, the top of the small hummocks were water-saturated during both the snowmelt period and single rainstorms, and subsequently fell dry, leading to a chemical signature comparable to that of the soil solution at upslope sites as was observed for the uppermost soil layer in another wetland of the same catchment (Lischeid et al., 2007). With respect to the third component, a high affinity of Al for DOC has been demonstrated in numerous studies (Helmer et al., 1990; Kerr et al., 2008; Olivie-Lauquet et al., 2001; Szkokan-Emilson et al., 2013). In waters with DOC $> 15\,mg\,l^{-1}$ – as was the case for the wetland and the Moorbach stream in our study – up to 100% of total Al was present as humate complexes (Viers et al., 1997). Thus, decomposition of these humate–Al–complexes could have resulted in a seasonally-variable export of both DOC and trace elements like Al from wetlands to streams. Higher Al concentration in stream water due to higher microbial activity in summer was also observed by other authors (Muller and Tankéré-Muller, 2012). To summarize, Clusters 1 and 2 seem to represent wetland waters discharging into the Moorbach stream influenced by more pronounced biogeochemical processes as compared to those influencing Cluster 3 in spring and early summer. This pattern was reflected in the Schöller classification mainly by decreasing NO_3, SO_4 and DOC and also by increasing Fe concentration (Fig. 8).

4.3. Cluster 4: rewetting after extensive groundwater level drawdown

Cluster 4 was observed after periods of extended groundwater level drawdown by more than 20 cm in summer and autumn (samples taken in early July 2005, August and October 2006; Fig. 6). The significant lower groundwater level and a significant lower antecedent cumulative precipitation (30 days period) seemed to be the most important differences as compared to Cluster 1, because there were no significant differences between these two clusters with respect to discharge, air temperature and residence time for the sampling dates (Fig. 7). In spite of that, the hydrochemical status in terms of the scores of the first two Isomap components and of most solutes (Figs. 4 and 5) differed the most between these two clusters, which was reflected in the Schöller and Piper classification as well (Figs. 8 and 9).

In 2007, not a single stream water sample was assigned to Cluster 4, although a similar drawdown of the groundwater level occurred in 2007 when compared to 2005 and 2006. However, groundwater drawdown and subsequent rewetting in 2007 occurred in early May; i.e., much earlier in the course of the year when compared to 2005 and 2006. This might indicate that microbial activity in April and in early May 2007 might not have been high enough to provide the conditions necessary for generating the stream water quality of Cluster 4. Obviously, memory effects have to be taken into account here.

Moorbach stream water samples characterized by this cluster reflected wetland water being highly influenced by oxic conditions (high scores of the first component, i.e., high NO_3 and SO_4 concentration, low Fe concentration) and by acidifying effects of historical SO_4 deposition (low scores of the second component, i.e., low DOC and Fe concentration, high SO_4 and Na concentration). Concurrently, a low influence of cation exchange or silicate weathering was observed (low scores of the third component). The results of the Piper and Schöller classification were in line with these findings (Figs. 8 and 9). Similar observations after drought periods were made, e.g., by Lamers et al. (1998), Szkokan-Emilson et al. (2013) and Watmough et al. (2016). Water level drawdown during drought periods can lead to oxidation of nitrogen (N), sulphur (S) and iron (Fe) species and to the concomitant release of protons in the upper soil layers in the wetland. Consequently, the upper soil layers can be acidified. Oxidized species like SO_4 and NO_3 could accumulate during the dry period in the upper soil layers and would be washed out during heavy rainstorms (Bechtold et al., 2003; Dillon and LaZerte, 1992; Eimers et al., 2007; Szkokan-Emilson et al., 2013; Zhang et al., 2010). Reoxidation of reduced S species was demonstrated for the wetland site in the Lehstenbach catchment (Alewell et al., 2006). Oxidizable sulphur originating from historical SO_4 deposition can lead to intensified acidification: the wetland receives anoxic groundwater from intermittent seeps and fens resulting in high amounts of Fe in the upper soil layers (Küsel and Alewell, 2004). In areas with a large Fe pool in the soil, historical SO_4 deposition strongly enhances FeS_x storage. An increased pool of FeS_x stimulates drought-related soil acidification, which influences the pH and causes an increase of potentially toxic metals like Al in pore water (Lamers et al., 1998). This relationship between acidification and Al release has been extensively investigated (e.g. Smolders et al., 2006; Szkokan-Emilson et al., 2013; Tipping et al., 2003; Watmough and Orlovskaya, 2015) and was in line with the high influence of Al-releasing weathering reactions found for Cluster 4.

4.4. Role of hydrological processes

In more than 80% of all cases, consecutive samples were assigned to the same cluster, pointing to rather stable biogeochemical conditions and only minor effects of hydrological processes in the short-term, i.e., within single stormflow events. This is in striking contrast to pronounced short-term chemical responses during stormflows observed in other streams of the catchment (Lischeid and Bittersohl, 2008; Lischeid et al., 2002; Strohmeier et al., 2013). However, in contrast to those streams, there is no well-buffered deep groundwater recharging the wetland stream that could be mixed in varying portions with near-surface runoff.

In winter, spring and early summer, runoff peaks did not change the cluster occurrence, i.e. the Moorbach stream water quality. This was true for a wide range of hydrological boundary conditions in the wetland, i.e. during water saturation conditions (April/May 2005, January 2007, April 2007) and after periods of extensive water level drawdown (> 20 cm; April 2007; Fig. 6), once the water level had recovered to complete saturation. Thus, the magnitude of discharge and base flow or storm flow conditions seemed to play a negligible role, as illustrated by the wide range of discharge during sampling for Clusters 1, 2 and 3 (Fig. 7). This observation pointed to rather stable chemical conditions in the wetland due to low microbial activity, which was in line with the results of Olivie-Lauquet et al. (2001).

Runoff events after periods of moderate groundwater level drawdown (less than 15 cm) in summer and autumn did not have a systematic influence on the cluster occurrence during or after the event on stream water quality. In some events, a shift from either Cluster 2 to Cluster 1 (or vice versa) with a quick shift back was observed. Thus, precipitation events after periods of moderate groundwater level drawdown can result in a decline or a peak of solute concentration of only short duration.

In contrast, stormflow after periods of extensive groundwater level drawdown (more than 20 cm) in summer and autumn systematically induced cluster changes from either Cluster 2 or 3 to Cluster 4, i.e. a substantial change of the stream water chemistry due to flushing of solutes that accumulated during the preceding drought period. Cluster 4 was observed for up to 28 days or longer after the precipitation event. Thus, extensive drought periods seem to have generated a high NO_3 and SO_4 export from the wetland to the Moorbach stream, despite reduced

sulphur deposition, combined with Al release.

These non-linear relationships between biogeochemical and hydrological processes have to be taken into account to produce reliable predictions of solute export with hydrochemical models used for water management purposes, especially with regard to the expected increasing frequency of drought periods due to climate change.

The residence time of the water seems to play an important role for the biogeochemical transformation within the wetland. Indeed, biogeochemical transformation rates are discussed to depend on the ratio between residence and reaction time scales (Oldham et al., 2013). This needs to be taken into account with regard to the impact of wetlands on water quality in the receiving streams.

4.5. Implications for single solutes

The interplay between the hydrological boundary conditions and the biogeochemical processes in the wetland via the microbial activity in the wetland turned out to determine the different types of Moorbach stream water samples. This interplay will be demonstrated below for NO_3 (positively correlated with the first Isomap component), DOC and SO_4 (positively and negatively correlated with the second Isomap component, respectively) and Al (negatively correlated with the third Isomap component).

NO_3 concentration usually follows the annual cycle of water table depth with a spring maximum and an autumn minimum (Aubert et al., 2013a; Prior and Johnes, 2002; Sponseller et al., 2014). However, NO_3 export in our catchment showed a much more complex pattern. This was presumably due to the interplay between water table position and microbial activity: as reflected by the change from Cluster 3 to Cluster 2, NO_3 export decreased from April to May 2005, although the water table remained near the soil surface (Figs. 5 and 6), likely due to enhanced microbial activity. NO_3 concentration near the detection limit represented by Cluster 1 was not limited to autumn runoff events as observed by Prior and Johnes (2002), but occurred e.g. in June or August due to enhanced microbial activity during periods of moderate groundwater level drawdown in the wetland (Fig. 6), and consequently, longer water residence time (Fig. 7). Periods of extensive groundwater level drawdown (Cluster 4), however, led to NO_3 concentrations similar to those in early summer (Cluster 2), even in the autumn months (Fig. 6). Similarly, Lupon et al. (2016) observed that NO_3 release from riparian wetlands was correlated with riparian evapotranspiration. Thus, the interplay between biogeochemical and hydrological processes has important implications for estimating the effect of wetlands for NO_3 retention, and its NO_3-removing capacity, and has to be taken into account in water management strategies.

DOC peaks in storm flow were ascribed to near-surface runoff during storms (Hagedorn et al., 2000; Hornberger et al., 1994; Inamdar et al., 2011; Mitchell et al., 2006), i.e., in the layer of highest DOC production (Cole et al., 2002). In the wetland studied here, however, DOC concentration in runoff showed high variation, although runoff was generated mainly in the topsoil layer. The highest DOC concentration was found for stream water samples represented by Cluster 1, followed by those represented by Cluster 2 (Fig. 5). Cluster 1 was characterized by discharge of wetland waters with the highest influence of anoxic redox processes, followed by Cluster 2 (Fig. 4). In contrast, declining DOC concentration and high SO_4 concentration occurred after periods of extensive groundwater level drawdown as reflected by the shift to Cluster 4 (runoff events beginning in July 2005, August, September and October 2006; Fig. 6), despite the water table rising up to the soil surface and topsoil water discharging to the Moorbach stream. In fact, during phases of high water tables, iron reduction was favoured and led to a concomitant DOC release. In contrast, during drought periods DOC concentration declined in the pore waters of the riparian wetland under study (Knorr, 2012) and elsewhere (Juckers and Watmough, 2014). A pattern inverse to that for DOC was observed for SO_4 (Knorr, 2012). These observations for the pore waters seem to be reflected in the Moorbach stream water samples as well, indicating that solute export from the wetland to the Moorbach stream depends on the antecedent moisture conditions controlling biogeochemical processes like redox reactions in the wetland. It is remarkable that a corresponding anticorrelation between the historical SO_4 deposition and DOC has been found elsewhere (Ledesma et al., 2016) and on a larger scale (Monteith et al., 2007).

A positive correlation between Al concentration and discharge was described in several studies (Kirchner, 2003; Piatek et al., 2009; Stutter et al., 2001). However, in our study, no such correlation could be observed. Aluminum concentration differed significantly between Clusters 1 and 4 (Fig. 5), although discharge did not (Fig. 7). In addition, Clusters 1 and 3 represented the highest and the lowest Al concentration, coming along with low and high discharge values, respectively. The Al concentration increased from Cluster 3 to Cluster 1 (Figs. 5 and 8), i.e., from winter to the summer months, following a seasonal pattern rather than discharge patterns. A similar seasonal pattern was observed by Muller and Tankéré-Muller (2012) and was related to higher microbial activity in summer. Thus, biogeochemical conditions related to water table position and season rather than discharge were essential for Al release to the Moorbach stream. Consequently, in catchments with a high proportion of wetland area, high Al concentration can be expected not only episodically during runoff peaks after drought periods, but over a longer period during the summer months. Higher air temperatures due to climate change will likely amplify Al release from wetlands to streams with consequences for water management strategies.

5. Conclusions

A Cluster Analysis of water quality data from a small stream draining a riparian wetland helped better understand the interplay between hydrological and biogeochemical processes in the wetland. Cluster analysis allowed a more detailed classification then the general classification using the Piper and Schöller diagrams. Solute export seemed to depend on the interplay between water table position and seasonally-varying biological activity, and thus varying biogeochemical conditions in the wetland. Temporal variability of stream water quality during single runoff events was negligible. Minimum biological activity and short residence time in the wetland hardly altered the quality of the groundwater that discharged into the stream during the dormant season. In contrast, increasing biological activity and increasing residence time in spring and summer had a major impact on wetland and stream water quality.

Periods with extensive groundwater level drawdown of more than 20 cm and subsequent rewetting led to a substantial increase of solute concentration and load (NO_3, SO_4, Na, Al) that lasted for up to 28 days or longer. However, that effect seemed to depend crucially on the intensity of microbial activity during the preceding period of groundwater level drawdown, pointing to a substantial biogeochemical memory effect.

Similar results are expected with respect to the Cluster Analysis for catchments with comparable geology, climate, land use and wetland proportion, i.e., for catchments with comparable biogeochemical processes and residence time in the wetland. However, each factor or process influencing the biogeochemical processes in a catchment, like another geology or land use, can also influence the results of the Cluster Analysis. In addition, further research would be required to investigate the effect of different catchment sizes on the interplay between biogeochemical and hydrological processes in order to improve the understanding of biogeochemical and hydrological dynamics on different scales of interest.

It is concluded, that biological activity in the riparian wetland, interacting with water table dynamics, proved to be a primary determinant of stream water quality and solute export. These non-linear relationships should be taken into account in biogeochemical modelling for improving predictions of stream water chemistry in water resources

management. More than a shift of annual mean values, single dry and warm periods are likely to predominate the dynamics and thus limit the retention capacity of wetlands and enhance solute export to the streams. A sound understanding of these dynamics is a necessary prerequisite for assessing the impact of both climate and land use change on stream water quality, nutrient export and carbon sequestration in riparian wetlands.

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Study 4

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Mineralogical sources of the buffer capacity in a granite catchment determined by strontium isotopes

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ABSTRACT

The role of different minerals in base cation release and thus the increase of buffering capacity of groundwater against acid deposition is controversially discussed in the literature. The $^{87}Sr/^{86}Sr$ ratios and base cation concentration were investigated in whole rock leachates, mineral separates, precipitation, soil solution, groundwater and stream water samples in the Lehstenbach catchment (Germany) to identify the weathering sequence of the granite bedrock. Three different approaches were followed in parallel. It was assumed that the contribution of different minerals to base cation supply of the groundwater with increasing weathering intensity would be observed by investigating (1) unweathered rock leachates, deep groundwater and shallow groundwater, (2) groundwater samples from new groundwater wells, reflecting the initial weathering of the drilled bedrock, and groundwater from wells that were drilled in 1988, (3) stream water during baseflow, dominated by deep groundwater, and stream water during high flow, being predominantly shallow groundwater. Whereas the first approach yielded consistent patterns, there was some evidence that groundwater from the new wells initially reflected contamination by the filter gravel rather than cation release in an initial stage of weathering. Time series samples of stream water and groundwater solute concentrations and isotope ratios turned out to reflect varying fractions of soil water and precipitation water at baseflow and high flow conditions rather than varying contributions of different minerals that prevail at different stages of granite weathering.

The early phase of weathering was clearly dominated by base cation release from biotite weathering and to a lesser extent by apatite dissolution. Feldspars contributed to base cation release as well, but could not be regarded as endmembers of the mixing diagram. There was no clear evidence for a contribution from calcite. Correspondingly, base cation input by atmospheric deposition and liming had only minor effects on groundwater buffer capacity.

1. Introduction

Acidification of soils, surface water and groundwater is still of major concern in silicate ecosystems, despite a significant reduction in acid deposition (H^+, S-compounds) in the last 20 a (Likens et al., 1998; Stoddard et al., 1999; Alewell et al., 2000; Busch et al., 2001; Armbruster et al., 2003; Matzner et al., 2004). Deep groundwater is usually less acidic than surface water (Neal et al., 1990a,b; Davies et al., 1992) due to release of base cations via weathering. Thus, deep groundwater plays an important role in the buffering of acid deposition (Reynolds et al., 1986; Cook et al., 1991). Similarly, an accidental groundwater change lead to long-lasting increases of pH (up to 1.5 pH units), alkalinity (up to 500 μE/L) and Ca concentrations (up to 9 mg/L) in

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the catchment runoff of a shallow soil catchment (Neal et al., 1997). During drilling, the loss of air-flush circulation resulted in the opening of groundwater fracture routes to the stream via the stream bed.

The buffering capacity of the bedrock depends on rate of release of base cations, i.e., the abundance and the weatherability of certain minerals. Reynolds et al. (1986) emphasized the effect of $CaCO_3$ in the bedrock on the buffering capacity of groundwater. Cook et al. (1991) traced the alkaline geochemistry of groundwater to dissolution of secondary vein calcite and to hydrolysis of silicate minerals. Moncoulon et al. (2004) concluded that the weathering rate in a catchment plays the most important part in soil buffering capacity. Weathering processes can be enhanced by acidic atmospheric inputs, as shown by Åberg et al. (1989), Likens et al. (1998, 2002) and Probst et al. (1999). In addition, atmospheric cation inputs might add to the geological source of buffer capacity (Moncoulon et al., 2004; Probst et al., 2000).

Chemical weathering models have been developed by many authors to investigate ecosystem sensitivity to acidic deposition (Christoffersen and Seip, 1982; April et al., 1986; Fritz et al., 1992; Probst et al., 2000). These models are usually based on the assumption that the most abundant minerals like plagioclase, K-feldspar, biotite and muscovite in granite bedrock are the major cation sources (Blum et al., 1994; Bullen et al., 1997; Négrel et al., 2001, 2003). Trace minerals such as calcite or apatite are often not taken into account. However, there is now increasing evidence that plagioclase is not the predominating geochemical Ca source in many acid rock catchments in spite of being the predominant Ca-bearing mineral (Clow et al., 1997; White et al., 1999; Jacobson and Blum, 2000; Négrel et al., 2003; Oliva et al., 2004). Thus, an additional Ca source is required to explain the observed chemical composition of the weathering solution. White et al. (1999) pointed out the role of disseminated calcite in the chemical weathering of granitoid rocks, using Ca/Na ratios compared to plagioclase stoichiometries and flow-through experiments. Likewise, Clow et al. (1997), Blum et al. (1998), Jacobson and Blum (2000) and Négrel et al. (2003) emphasized the contribution of calcite present in trace amounts in silicate bedrock (gneiss, granite) to the chemical composition of the weathering solution. Oliva et al. (2004) attribute more than 90% of the Ca export from high elevation watersheds in the Pyrenees (France) to the dissolution of apatite and other trace Ca-rich minerals, representing less than 1% of the total rock volume. Similar results were found by Aubert et al. (2002) and Blum et al. (2002). Harlavan and Erel (2002) observed preferential release of Pb and rare earth elements from some accessory phases (i.e. allanite, sphene and apatite) during granitoid weathering.

$^{87}Sr/^{86}Sr$ ratios have been used in geology to determine the age and the origin of rocks (Faure, 2001). Now they are increasingly used to identify Ca sources due to the similar chemical behaviour of Sr and Ca (Åberg et al., 1989; Gosz and Moore, 1989; Wickman and Jacks, 1992; Miller et al., 1993; Bailey et al., 1996; Clow et al., 1997). Åberg et al. (1989), Wickman and Jacks (1992), Bain and Bacon (1994), Clow et al. (1997), Probst et al. (2000), Harrington and Herczeg (2003) studied weathering processes and Frape et al. (1984), Kay and Darbyshire (1986), Négrel et al. (2003) and Gosselin et al. (2004) water–rock interactions in watersheds using Sr isotope ratios. The impact of atmospheric inputs on water quality in watersheds was investigated by Graustein and Armstrong (1983), Gosz and Moore (1989) and Probst et al. (2000). A summary concerning the methodology of Sr isotopes in general and the use of Sr isotopes to identify hydrological and hydrogeochemical processes in watersheds is given e.g. in Bullen and Kendall (1998).

In the present study, $^{87}Sr/^{86}Sr$ ratios and major and trace elements were determined in a granite catchment in order to ascertain the mineralogical sources of the buffer capacity. To that end, different parallel approaches that were assumed to give the same results were followed. First, leaching experiments were performed with unweathered rock samples and the chemical and isotopic composition of separated minerals were determined. Second, groundwater samples from different sites and different depths were analysed as well as rain water, soil solution and stream water on different dates. Third, groundwater samples from wells, that were installed in 1995 and 1996 and that exhibited very high and steadily decreasing Ca concentration, were compared to wells that were drilled in 1988. The enhanced Ca concentration of the new installed wells was traced back to enhanced base cation release after drilling of the unweathered bedrock. Thus, it was hypothesized that the degree of contribution of different minerals to base cation supply of the groundwater with increasing weathering intensity would be observed by investigating

(1) unweathered rock leachates, deep groundwater and shallow groundwater,
(2) groundwater samples from new groundwater wells, reflecting the initial weathering of the drilled bedrock, and groundwater from wells that were drilled in 1988,
(3) stream water during baseflow, predominantly deep groundwater, and stream water during high flow, being predominantly shallow groundwater.

2. Site description

The study was performed in the Lehstenbach watershed (50°08′N and 11°52′E) in the Fichtelgebirge Mountains in SE Germany (Gerstberger et al., 2004). The watershed area is 4.19 km^2 and elevation ranges from 690 m to 877 m a.s.l. (Fig. 1).

Bedrock is variscan granite of two different facies: the fine-grained Outer Granite having a porphyritic structure and the middle- to coarse-grained Core Granite (Stettner, 1964). The Outer Granite is 291 ± 7 Ma and the Core Granite of 288 ± 4 Ma (Besang et al., 1976). The two facies show very similar mineralogical composition: the predominant minerals are quartz (36%), K-feldspar (29–38%) and plagioclase (17–24%).In addition, biotite and muscovite comprise another 8–10%. Less than 0.5% of the total volume is due to accessory minerals, including apatite.

The thickness of the regolith is very heterogeneous, and exceeds 40 m at many sites in the catchment due to intensive tertiary weathering (Lischeid et al., 2002). The area

was not glaciated during the pleistocene. Drilling profiles down to 27 m depth show an irregular interlayering of sandy to sandy-loamy grus, strongly weathered granite and some massive boulders up to several meters in diameter. Dystric cambisols and podzols predominate. In the riparian zone, fibric histosols and dystric gleysols are found, representing about one third of the watershed area. Soils are strongly acidified showing a pH(H_2O) in the A-horizon as low as 3.70 (Gerstberger et al., 2004). The climate is humid-continental, annual mean air temperature is 5.75 °C and annual mean precipitation is between 950 and 1250 mm. Dense Norway spruce stands cover more than 95% of the watershed area.

Groundwater circulates mainly in the regolith that can be considered as a porous aquifer with a saturated hydraulic conductivity of 3×10^{-6} m s^{-1} (Lischeid et al., 2002, 2004a). Mean groundwater level is close to the surface during the whole year in the riparian zone and more than 10 m below the surface in the upper part of the catchment. Amplitudes of groundwater level variations are less than 1 m in the riparian zone and more than 5 m in the upper part of the catchment. There are 13 observation wells in the catchment gauged down to 10 m depth at least, but no production wells. Seven out of these wells were installed 1995 and 1996. Some of these wells initially exhibited very high Ca concentrations that clearly decreased during subsequent years. It was speculated that drilling might have enhanced access to unweathered Ca-bearing minerals in the solid granite rock, leading to substantial release of additional buffer capacity of the groundwater. In addition, shallow piezometers were installed at different wetland sites in the watershed.

The area is drained by a dense network of natural streams and artificial channels, some of which are ephemeral, especially in the upper part of the catchment. Mean residence time of water measured at the catchment outlet is 3.6 a. Mean annual runoff is 461 mm (1988–1999) (Lischeid et al., 2002). Groundwater flow in the regolith parallel to the stream at the catchment outlet is therefore likely to play a negligible role in the total outflow (Lischeid et al., 2002). Stream discharge is generated by deep groundwater recharge during baseflow conditions and does not fall below 0.25 mm per day even during longer dry periods. During heavy rainstorms the riparian zone is saturated to the surface, thus hydrologically connected to the stream which can explain the strong increase (10–20 fold over baseflow) in stream discharge during heavy rainstorms (Lischeid et al., 2002).

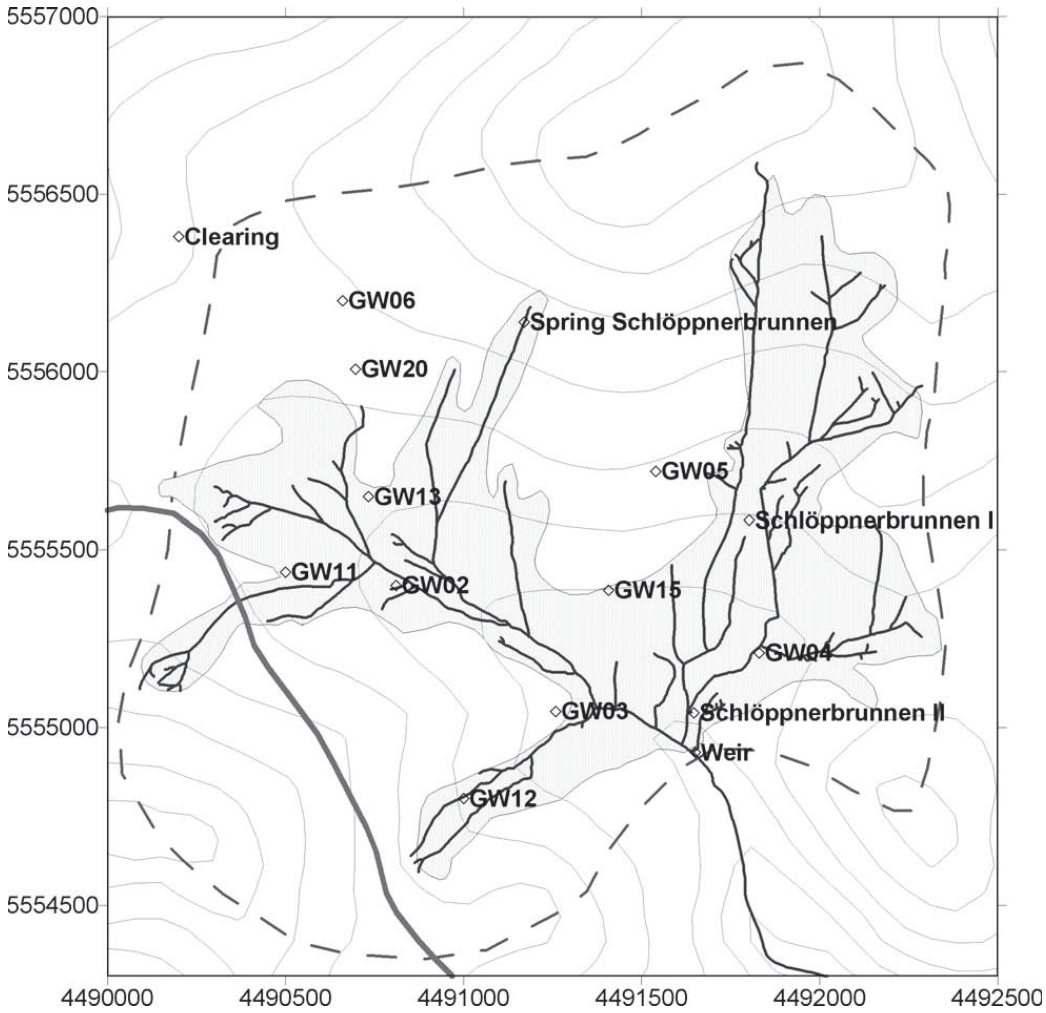

Fig. 1. Map of the Lehstenbach watershed in the Fichtelgebirge mountains in SE Germany. Gauss–Krüger coordinates [m] are given on the axes.

Table 1
Compilation of sampling sites and water sampling scheme (number of samples per period)

Component	Sampling site	Groundwater table (m below ground surface)	Screening zone (m)	End of baseflow 2002 21/22 October	Transition period 2002 19 November	After rewetting 2002 03/06 December	End of high water period 2004 24 May	High water period 2005 21 March
Groundwater at wetland sites	GW02	0–1	1–10					1
	GW04	0–1	2.3–14.3	1		1	1	1
	Schlöppnerbrunnen I (1 m)[a]	0–1	0.9–1	1		1		
	Schlöppnerbrunnen I (2 m)[a]	0–1	1.9–2	1		1		
	Schlöppnerbrunnen II (1 m)[a]	0–1	0.9–1	1		1		
	Schlöppnerbrunnen II (2 m)[a]	0–1	1.9–2	1		1		
	Schlöppnerbrunnen II P1.1	0–1	0.9–1					1
	Schlöppnerbrunnen II P1.2	0–1	1.9–2					1
	Schlöppnerbrunnen II P2.1	0–1	0.9–1					1
	Schlöppnerbrunnen II P2.2	0–1	1.9–2					1
	Schlöppnerbrunnen II P3.1	0–1	0.9–1					1
	Schlöppnerbrunnen II P3.2	0–1	1.9–2					1
Groundwater at upslope sites	GW01	2–9	3–15					1
	GW03a	0–4	2–15.4	2[c]		2[c]	1	1
	GW03b	0–4	2.2–3.2					1
	GW05	9–16	5.3–24.3					1
	GW06	3–9	4–16	2[c]		2[c]	1	1
	GW11	0–4	7.5–10.5					1
	GW12	0–5	7–10					1
	GW13a	0–6	7–10					1
	GW13c	0–1	1–2					1
	GW15a	2–8	7–10					1
	GW17	3–7	7–10				1	1
	GW20a	0–4	7.5–10.5				1	1
	GW20b	0–4	0.85–1.35					1
	GW20c	0–4	0.35–0.85					1
Soil solution	GW03		0.9	1	1			
	GW06		0.9	1	1			
Discharge	spring Schlöppnerbrunnen			1		1		1
	Weir			4	2	1		1
Bulk precipitation	clearing Weidenbrunnen[b]			1	1	1		
Throughfall	GW03[b]			1	1	1		
	GW06[b]			1	1	1		

[a] Merged samples from 3 piezometers.
[b] Merged samples from 15 samplers.
[c] Two samples taken from the top and bottom part of the groundwater well.

The watershed is still highly affected by atmospheric deposition (S oxides, N oxides, protons, base cations) that peaked in the 1970s and steadily decreased thereafter (Matzner et al., 2004). Due to the decreasing SO_4 deposition, SO_4-concentration in the topsoil has shown a decreasing trend, whereas in the groundwater no clear pattern of concentration trends was observed (Lischeid et al., 2004a). In contrast, pH and alkalinity of runoff were closely correlated to discharge and decreased during high flow conditions to 3.9 and -0.1 m $mol_c\,L^{-1}$, respectively (Lischeid et al., 2004a). The catchment has been limed with dolomite several times in the past, excluding the riparian zone. In general, Ca and Na are the predominant cations in streams and groundwater (Lischeid et al., 2004a).

3. Methods

3.1. Sampling

Groundwater, soil solution, precipitation and runoff were sampled at different sites in the catchment in order to investigate temporal and spatial variability of Sr isotope ratios and solute concentrations (Fig. 1, Table 1). Sampling dates were selected to represent the hydrological periods: end of baseflow (October 2002), a hydrological transition period (November 2002), after rewetting of the catchment (December 2002), end of a high water period (May 2004) and during a high water period (March 2005). Groundwater was sampled at wetland and hillslope sites at different depths (Table 1). Groundwater from the upper part of the aquifer was sampled by a pump submerged 1 m below the groundwater table (GW03a, GW06) and 1 m above the lower end of the gauge (GW01, GW02, GW03a, GW04, GW06, GW11, GW12, GW13a, GW17, GW20a). A low pumping rate (0.05 L s^{-1}) was used in order to avoid mixing of the water in the well. At the sites Schlöppnerbrunnen I and II, GW03b, GW13c, GW20b and GW20c groundwater was sampled in piezometers with a submerged pump. At Schlöppnerbrunnen I and II, samples from 3 piezometers each gauged at 1 m and 2 m depths, respectively, were merged.

Suction cups at 1 m depth collected soil solution at sites GW03 and GW06. At each site, soil solution from several suction cups yielded an aggregated sample. The vacuum was maintained between -200 and -300 hPa (Lischeid et al., 2002). Stream discharge at the catchment outlet was recorded every 10 min. Water samples were taken at hourly intervals by an automatic sampler, but only selected samples were analysed. The Schlöppnerbrunnen spring was sampled manually on two dates. Open field precipitation was collected over 14-day periods at a clearing close to the watershed boundary at 765 m a.s.l. (Fig. 1), and throughfall was collected at sites GW03 and GW06. At each site, precipitation collected in 15 rain collectors was merged to yield an aggregated sample per date and site.

Samples of plagioclase and K-feldspar were obtained from a crushed unweathered Core Granite sample. The 0–200 μm fraction of the crushed rock was sieved to give a 100–200 μm fraction. A plagioclase and a K-feldspar sample were obtained using magnetic, heavy liquids and hand picking techniques. The purity of the mineral separates was tested by visual inspection using a binocular microscope. Due to the very similar density of plagioclase (2.63–2.66 g cm^{-3}) and quartz (2.65 g cm^{-3}) in the sample, it was not possible to separate the two mineral types. Therefore, the number of plagioclase grains in three times 100 mineral grains was determined under a binocular microscope and the mean percentage of plagioclase and quartz in the sample was calculated. Mineral separates were digested in sealed Teflon vessels using high-purity HNO_3, HF and HCl. The Teflon vessels remained on a heating plate for several days. The ICP-MS analysis of the mineral samples was additionally validated by analysing 100 mg of the CRPG Biotite Mica-Fe standard and of the ANRT K-feldspar FK-N standard and a replicate, respectively, that were digested as were the mineral samples.

Trace minerals such as apatite or microcrystalline calcite could not be separated from the bedrock because of their extremely small grain size. In other studies, trace minerals were at least semi-quantitatively identified by XRD (e.g. Jahnke, 1984; Valsami-Jones et al., 1998). In the present study, however, samples from the drill cores at GW17 (P17) and GW20 (P20) that were taken from 3 depths (3–4 m, 6–7 m, 9–10 m) were used for sequential leaching experiments to chemically extract easily soluble trace minerals from the bedrock according to the method of Clow et al. (1997). 150 g of crushed and sieved (<2 mm) granite of each sample were leached with 150 mL of deionized water in three sequential steps. For each step, samples were shaken for 1 h, centrifuged, decanted and filtered through a 0.2 μm cellulose-acetate-membrane filter and stored in polyethylene bottles in the dark at less than 4 °C.

The same procedure was used for a sequential leaching experiment with a sample of the dolomite used for liming of the catchment. Because of the greater sample volume compared to that of trace minerals in the granite, only 20 g dolomite were shaken with 90 mL deionized water.

3.2. Chemical analysis

Water samples were filtered through 0.45 and 0.2 μm cellulose-acetate-membrane filters, respectively. They were stored in polyethylene bottles in the dark at less than 4 °C until further analysis. Major and trace element concentrations of water and mineral digests were determined by ICP–MS (HP4500®) and are precise to within 1 and 3%. Major element concentrations of sequential leaching experiment samples were determined by ICP–OES (Varian Vista-Pro CCD Simultanous), and trace element concentrations by ICP–MS (Agilent 7500 ce).

Strontium was separated from water, digested minerals and from sequential-leach experiments samples using Sr-SPEC (EiChrom Industries, 100–150 μm) and Dowex AG 50 W-X8 (200–400 mesh, Bio-Rad®) resin. $^{87}Sr/^{86}Sr$-ratios were determined by mass spectrometry (Finnigan MAT 262). Isotope ratios have been corrected for natural and analytical stable isotope fractionation to $^{88}Sr/^{86}Sr = 8.375209$ and for ^{87}Rb-traces, with the same mass as ^{87}Sr to $^{85}Rb/^{87}Rb = 2.59265$. $^{87}Sr/^{86}Sr$ ratios are precise to within 6×10^{-6}–26×10^{-6} (2σ, standard error). The NIST 987

standard yielded values of 0.710217 ($n = 33$; $2\sigma = 32 \times 10^{-6}$) and 0.710241 ($n = 14$; $2\sigma = 6 \times 10^{-6}$) for water samples, 0.710159 ($n = 4$; $2\sigma = 5 \times 10^{-6}$) for mineral digest samples and 0.710253 ($n = 11$; $2\sigma = 7 \times 10^{-6}$) for sequential leaching experiment samples.

3.3. Principal component analysis

It was assumed that the water samples represented varying fractions of single endmembers. In order to determine these endmembers a principal component analysis (PCA) was performed using data from different sources. The data set comprised (1) Ca, Mg, Ba, Na, K, Sr and Rb concentrations and $^{87}Sr/^{86}Sr$ ratios of the water samples, digested mineral samples and sequential leachate samples of the study, (2) Ca, Mg, Ba, Na, K, Sr and Rb concentrations of leachates from Irber (1996) and Irber et al. (1997) using samples from the Lehstenbach catchment and granite samples from other sites in the Fichtelgebirge Mountains and in the Ore Mountains (East Germany) and (3) Ca, Mg, Ba, Na, K and Rb concentrations of digested mineral samples from the Bohemian Massif, the Fichtelgebirge mountains and the nearby Mitterteich granites from Siebel (1995) and Siebel et al. (1997). There were no Sr isotope ratios available for these biotite samples. Assuming that the $^{87}Sr/^{86}Sr$ ratio of biotite is always highly radiogenic, a notational Sr isotope ratio of 5.00 was used for these samples. The concentrations in groundwater samples and from the different leaching experiments were not comparable due to different methodologies. Besides, not all elements were analysed in all of the studies. Thus, it was not possible to use concentration ratios. Instead, the data were normalised using Eq. (1). The element concentration data were divided by the mean values of the respective dataset. Then the mean value of all these quotients for one author was calculated. This value was used to divide every element concentration given by the author. Data were then log transformed in order to obtain a Gaussian distribution and z-standardised with respect to the whole dataset (mean value = 0, standard deviation = 1) Eq. (2).

$$c_{x,\mathrm{norm}} = \frac{c_x}{\frac{1}{n} \cdot \sum_n c_x} \tag{1}$$

where $c_{x,\mathrm{norm}}$ is the normalised concentration of element x; c_x is the concentration of element x; $\frac{1}{n}\sum_n c_x$ is the mean of the concentrations of all n elements from one dataset used for the PCA (i.e. datasets of mineral leaching, water samples, minerals from the present study, the dataset from Irber (1996) and Irber et al. (1997) and the dataset from Siebel (1995) and Siebel et al. (1997))

$$c_{x,\mathrm{stand}} = \frac{\log(c_{x,\mathrm{norm}}) - \frac{1}{n}\sum_n \log(c)_{n,m}}{\mathrm{SD}(\log(c)_{n,m})} \tag{2}$$

where $c_{x,\mathrm{stand}}$ is the z-standardised concentration of element x; $\frac{1}{n}\sum_n \log(c)_{n,m}$ is the mean of the concentrations of all n elements from all m datasets used for the PCA; $\mathrm{SD}(\log(c)_{n,m})$ is the standard deviation of the concentrations of all n elements from all m datasets used for the PCA.

Principal components with an eigen value greater than 1 were extracted, using a varimax rotation.

3.4. Saturation indices

For all samples from groundwater outside the wetlands the saturation indices (SI) with respect to biotite, feldspars and apatite were calculated based on the chemical equilibria (3)–(6). Albite and K-feldspar were used as corresponding endmembers of the feldspar mixing series

$$\text{Biotite}: \ KAl_3Si_3O_{10}(OH)_2 + 10H^+ \rightarrow K^+ + 3Al^{3+} + 3H_4SiO_4 \quad \log K_{sp} = 12.703 \tag{3}$$

$$\text{Albite}: \ NaAlSi_3O_8 + 8H_2O \rightarrow Na^+ + Al(OH)_4^- + 3H_4SiO_4 \quad \log K_{sp} = -18.002 \tag{4}$$

$$\text{K-feldspar}: \ KAlSi_3O_8 + 8H_2O \rightarrow K^+Al(OH)_4^- + 3H_4SiO_4 \quad \log K_{sp} = -20.573 \tag{5}$$

$$\text{Apatite}: \ Ca_5(PO_4)_3OH + 4H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + H_2O \quad \log K_{sp} = -3.42 \tag{6}$$

The ionic activity products (IAP) were calculated using Eq. (7), the saturation indices (SI) using Eq. (8). The solubility product values ($\log K_{sp}$) for the different minerals were taken from the USGS Software FREEQC. The saturation index with respect to calcite could not be calculated due to the lack of hydrogen carbonate data.

$$\mathrm{IAP} = \prod a_x^n \tag{7}$$

where IAP is the ionic activity product, and a is the ionic activity of the dissolved species x and n the stoichiometric number

$$\mathrm{SI} = \mathrm{pK_{sp}} - \mathrm{pIAP} \tag{8}$$

4. Results

As will be shown in this section, three different groups of groundwater wells could be discerned: The wetland group (wetland wells) comprises predominantly shallow groundwater wells in the wetland areas that have very low O_2 concentration (not shown). This group consists of the wells Schlöppnerbrunnen II, Schlöppnerbrunnen I (1 m) and wells GW02 and GW04. The second group comprises predominantly deep groundwater wells at upslope sites that were mostly installed in 1987–1988 (deep groundwater group I) (old wells), that is, the wells GW01, GW03a and GW06. The wells of the last group resemble those of the second group with respect to gauging depth, upslope location and O_2 concentration of the groundwater samples. However, these wells were installed in 1995 or later. This group will be named the deep groundwater group II (new wells). It consists of the wells GW11, GW12, GW13a, GW13c, GW17, GW20a, GW20c and Schlöppnerbrunnen I (2 m). The results will be presented for the three groups.

4.1. Single solutes

The percentiles of mean groundwater solute concentration are presented for the 2003–2005 period (Fig. 3). Sig-

nificant trends could be identified only at some single wells (Lischeid et al., 2004a), but not for whole groups. The pH values of groundwater group I are around 5, and those of the deep groundwater group II and of the wetland group around 6. Due to long-lasting atmospheric deposition, SO_4 is the prevailing anion in the groundwater samples (Lischeid et al., 2004a). Sulfate concentration in the wetland wells is substantially less compared to the remaining wells, which is traced back to dissimilatory SO_4 reduction as well as to the effect of decreasing SO_4 deposition since the late 1970s (Lischeid et al., 2004a). Correspondingly, decreasing deposition presumably led to lower Ca and Mg concentrations in the shallow wetland wells. In addition, liming of the forest soils with dolomite was restricted to the upslope sites. It is remarkable that the deep groundwater group II exhibits the highest Ca concentrations, and also the highest range of Ca contents. The same holds for Mg, although to a lower degree.

The highest Ca concentrations were observed in the groundwater of wells GW11, GW12, GW17 and GW20a after drilling in 1995 and 1996 and decreased substantially later in 3 of the wells (Fig. 2). This effect was much more pronounced in well GW20a than in well GW12 and GW17. In well GW13a, that is located downstream of GW20a (Fig. 1), Ca concentrations started to increase as soon as they decreased in well GW20a. High Ca concentrations were associated with high Mg and SO_4 concentrations and high pH values (not shown).

4.2. $^{87}Sr/^{86}Sr$ ratios and Sr concentrations

Strontium isotope ratios are plotted in the form of a Keeling diagram versus the reciprocal Sr concentrations (1/[Sr]) in Fig. 4. In this representation, mixing of a constant background component with a component with varying concentration would yield a straight line (Faure, 2001). The three groundwater groups could clearly be differentiated based on $^{87}Sr/^{86}Sr$ ratios and Sr concentrations.

Samples from the deep groundwater group I exhibited high $^{87}Sr/^{86}Sr$ ratios and high Sr concentrations. They clearly differed from those of the deep groundwater group II with low $^{87}Sr/^{86}Sr$ ratios and high Sr concentrations. The Sr isotope ratios of the deep groundwater group I were very close to or slightly exceeding those of plagioclase. In contrast, the deep groundwater group II showed Sr isotope ratios similar to those of the apatite and dolomite leach samples, especially at well GW20a. Most of the leach samples showed Sr isotope ratios ranging between those of apatite and precipitation to the values of plagioclase (Fig. 6). There was no clear relationship with depth or number of sequential leaching steps. The $^{87}Sr/^{86}Sr$ ratios of the dolomite used for liming of the catchment increased during the sequential leaching experiment from $0.708051 \pm 6 \times 10^{-7}$ to $0.708142 \pm 8 \times 10^{-7}$ (Fig. 4).

The samples from the wetland group are characterized by low $^{87}Sr/^{86}Sr$ ratios and low Sr concentrations. In addition, soil solution samples of sites GW03 and GW06 plot in this field. Moreover, the wetland samples were close to those of precipitation and throughfall.

Stream water samples from the catchment outlet plot between the three groundwater endmembers (Fig. 4). The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in the Lehstenbach catchment runoff decreased during stormflow in October 2002 compared to baseflow (Fig. 5). The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in the runoff of the Schlöppnerbrunnen spring were intermediate between those of the two deep groundwater components. There are no wetlands in the subcatchments of that spring.

Strontium isotope ratios and concentrations of the groundwater wells as well as the precipitation samples

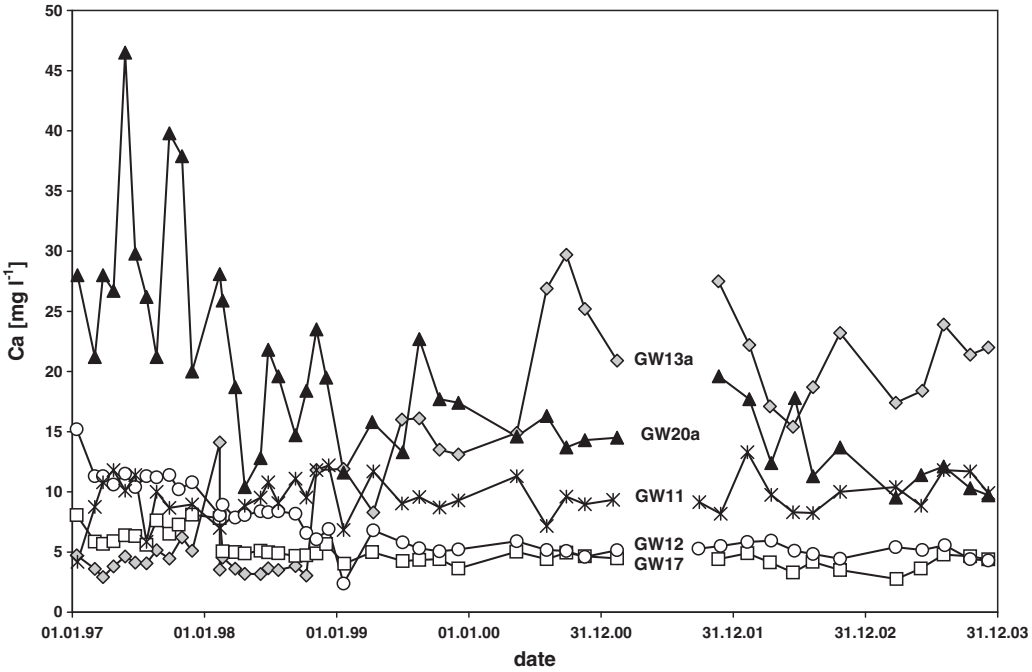

Fig. 2. Time series of Ca concentrations [mg L^{-1}] in groundwater wells GW11, GW12, GW13a, GW17 and GW20a from 1997 to 2003. The lack of data for the April and September sampling dates 2001 is due to analytical problems.

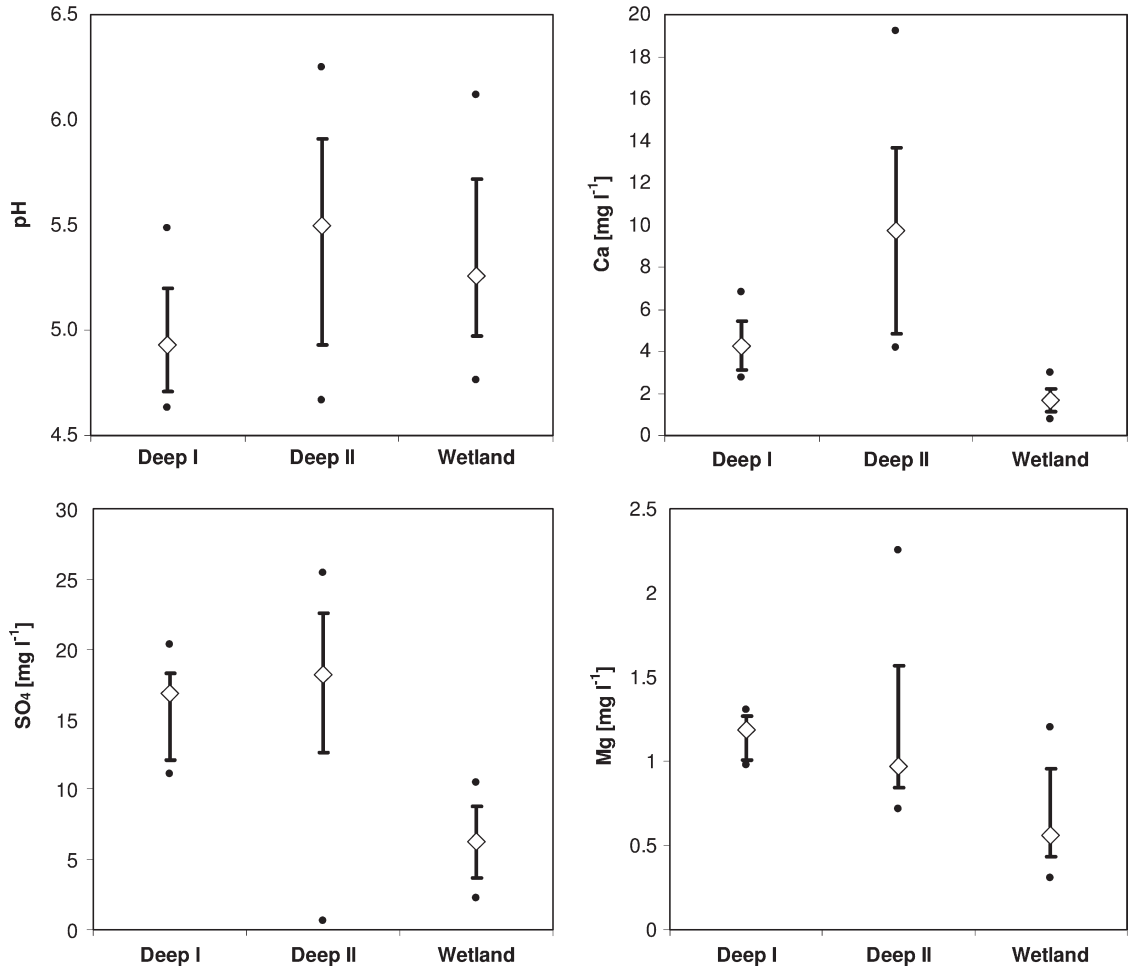

Fig. 3. Quartiles, 10% and 90% percentiles of pH, SO_4, Ca and Mg concentrations for the deep groundwater group I (deep I), deep groundwater group II (deep II) and wetland groundwater (wetland). SO_4, Ca and Mg concentrations are in mg L^{-1}.

did not show any consistent temporal pattern and will not be discussed here.

4.3. Cation ratios and saturation indices

The Ca/Na ratios of plagioclase were higher than those of K-feldspar. Ca and Na concentrations of muscovite and biotite were not available. The Ca/Na ratios of the dolomite varied from 6.42 to 20.12 (Fig. 6).

The Ca/Na ratios of most of the water samples were higher than those of plagioclase (Fig. 6). In general, there is a clear tendency of low Ca/Na ratios in the wetland groundwater wells, and higher ratios in the two deep groundwater groups. The deep groundwater group II exhibited the largest variance, with the highest Ca/Na ratios in wells GW13a and GW20a of this group. Nearly all leach samples except for P17 (3–4 m) and P20 (6–7 m) had Ca/Na ratios lower than those of all water samples and lower than those of plagioclase and biotite. In particular, they were lower than those of apatite by a factor up to nearly 25,000.

The groundwater samples from upslope sites were highly undersaturated with respect to biotite (SI = −21 ± 1.4, n = 28) and apatite (SI = −10 ± 1.7, n = 25) but highly oversaturated with respect to K-feldspar (SI = 12 ± 1.4, n = 28) and albite (SI = 10 ± 1.3, n = 28). There was no difference of saturation index values between deep groundwater groups I and II.

4.4. Principal component analysis

The objective of the principal component analysis was to enable an integrated interpretation of the results considering all solutes that were analysed simultaneously. Moreover, data from earlier studies were included, partly from the same region. Due to the normalization of the datasets, factor values of the samples can only be interpreted with respect to the distance of a data point to the 1:1 mixing line. Interpretations along parallels to this line can only be done for water samples.

Two principal components with eigen values greater than one were extracted that explained 66.8% of the variance. The first principal component was mainly determined by Sr, Ca, Na, Ba and to a lesser extent by Mg and the reciprocal $^{87}Sr/^{86}Sr$ ratio, the second principal component by K, Rb, and to a lesser extent by Mg and Ba and the $^{87}Sr/^{86}Sr$ ratio (Fig. 7).

The factor values of the two principal components are given in Fig. 8. In general, values of the first and second principal component increased from precipitation (open field precipitation and throughfall) and soil solution via wetland groundwater to deep groundwater. The two prin-

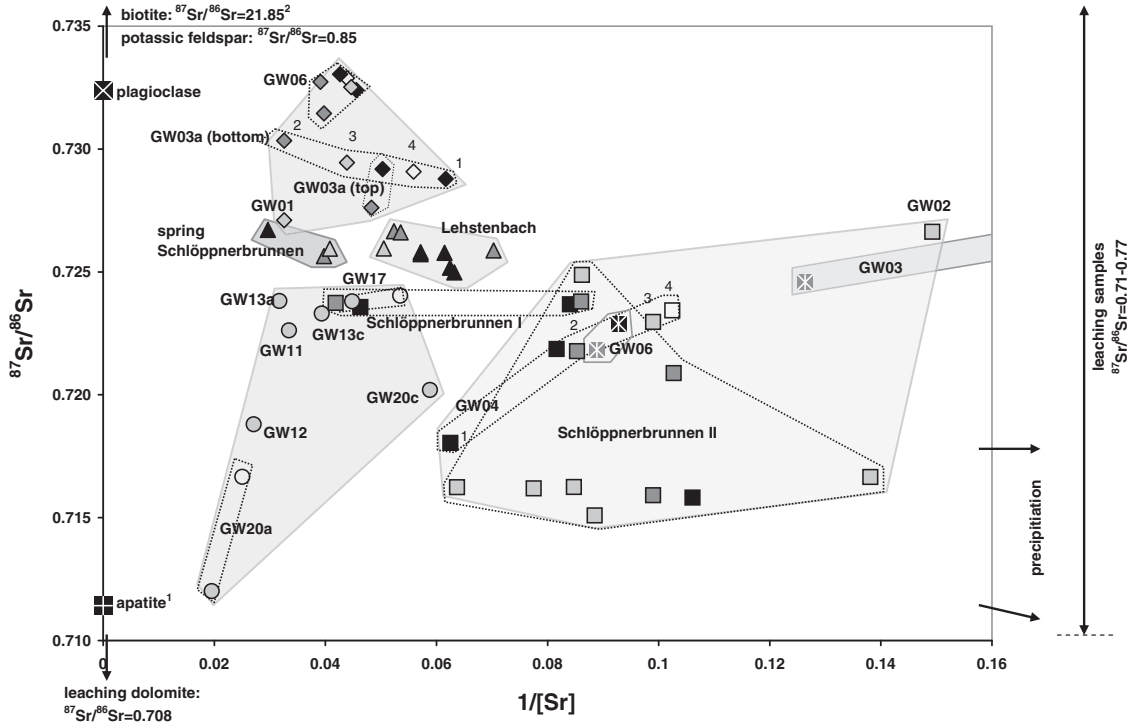

Fig. 4. $^{87}Sr/^{86}Sr$-ratios versus reciprocal Sr concentrations (Keeling diagram) of water, mineral and leaching experiment samples. Black symbols: end of baseflow (2002) (21/22 October), dark grey symbols: transition period (2002) (19 November) and after rewetting (2002) (03/06 December), light grey symbols: high water period (2005) (21 March), open symbols: end of high water period (2004) (24 May). For better visibility, the data points representing the three groundwater groups, catchment runoff, spring runoff and soil solution are underlaid in grey, the data points representing different sampling dates of the same groundwater sampling site are delineated with dotted lines. Schlöppnerbrunnen I and II represent different piezometers of 1 and 2 m depth. (see Table 1). [1]Irber (1996) [2]Besang et al. (1976), sample B624, core granite.

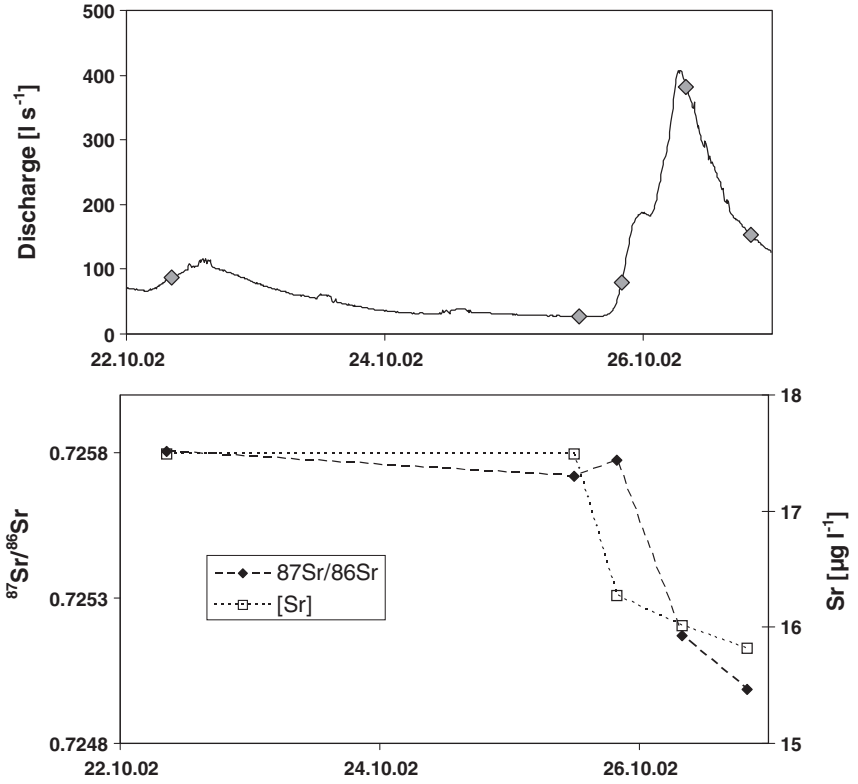

Fig. 5. Sampled discharge peak of the Lehstenbach stream between the 22nd and the 26th October 2002. (a) Discharge; diamonds denote the sampling dates. (b) $^{87}Sr/^{86}Sr$-ratios and Sr concentrations [$\mu g\,L^{-1}$].

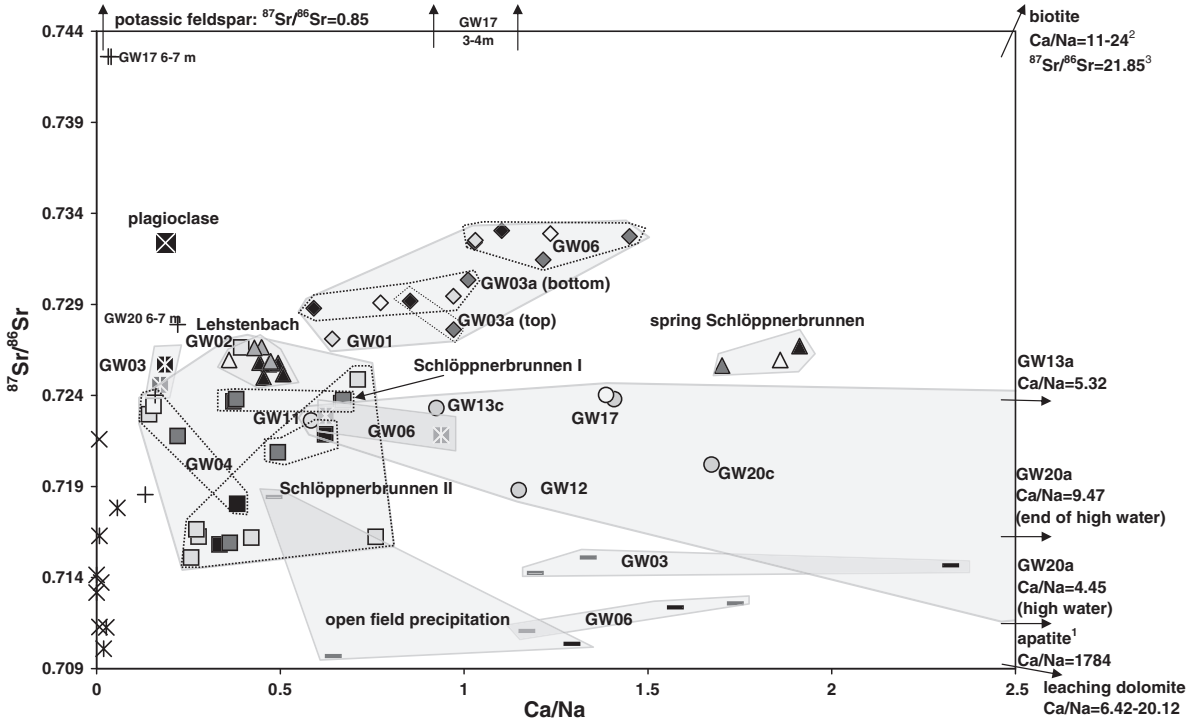

Fig. 6. $^{87}Sr/^{86}Sr$-ratios versus Ca/Na ratios of water, mineral and leaching experiment samples. Black symbols: end of baseflow (2002) (21/22 October), dark grey symbols: transition period (2002) (19 November) and after rewetting (2002) (03/06 December), light grey symbols: high water period (2005) (21 March), open symbols: end of high water period (2004) (24 May). Rock leachates 3–4 m, 6–7 m and 9–10 m represent rock leachates from both drill cores from wells GW17 and GW20. For better visibility, the data points representing the three groundwater groups, catchment runoff, spring runoff, soil solution, throughfall and open field precipitation are underlaid in grey, the data points representing different sampling dates of the same groundwater sampling site are delineated with dotted lines. Schlöppnerbrunnen I and II represent different piezometers of 1 and 2 m depth (see Table 1). [1] Irber (1996) [2] Irber (1996), granite samples leaching experiments of 2, 5 and 20 h [3] Besang et al. (1976), sample B624, granite core.

cipal components allowed delineation of precipitation from groundwater, mostly due to higher values on the first principal component of the latter (Fig. 8). Wetland groundwater with lower values on the second principal component and slightly lower values on the first can clearly be distinguished from groundwater outside the wetlands (deep groundwater groups I and II). The samples of deep groundwater group I show considerable overlap with the deep groundwater group II. Catchment runoff samples had an intermediate position between wetland groundwater on the one hand and the two deep groundwater groups on the other hand. Spring runoff plotted in the field of deep groundwater groups I and II (Fig. 8).

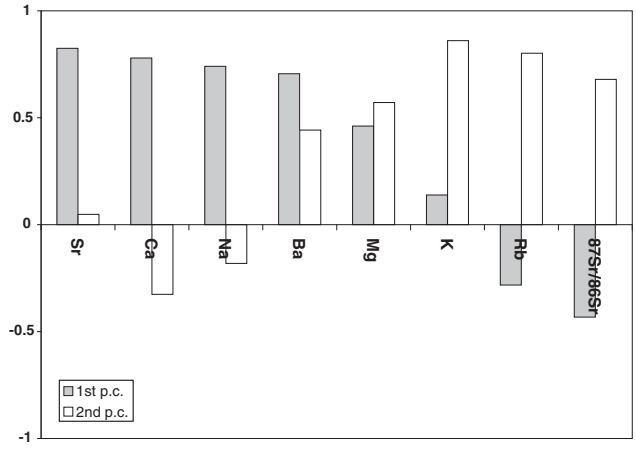

Fig. 7. Loadings of the parameters used for the PCA on the three principal components (pc).

Based on this analysis, biotite could be clearly identified as an endmember. Most of the biotite samples showed the highest factor values for the second principal component (Fig. 8) due to high concentrations of K, Rb and Mg and high $^{87}Sr/^{86}Sr$ ratios. On the other hand, the apatite leach samples from Irber (1996) and the first leaching step sample from the dolomite leach had high factor values of the first principal component, due to high Ca, Na and Sr values and low $^{87}Sr/^{86}Sr$ ratios. In contrast to dolomite, that plot in the range of groundwater, the distance of apatite leaching samples from the 1:1 mixing line was greater than that of all water samples. Thus, apatite could be considered as an endmember. The plagioclase and K-feldspar sample from the granite in the Lehstenbach catchment and the albite and K-feldspar leach samples from Irber (1996) plot between the biotite and the water samples and could thus not be considered as endmembers.

5. Discussion

The discussion is organized as follows: In the first section the methodology of the leaching experiments will be compared to that of other studies. Second, additional sources of base cation release beside weathering will be evaluated. Third, the three different approaches to identify the weathering sequence will be discussed. In the last sec-

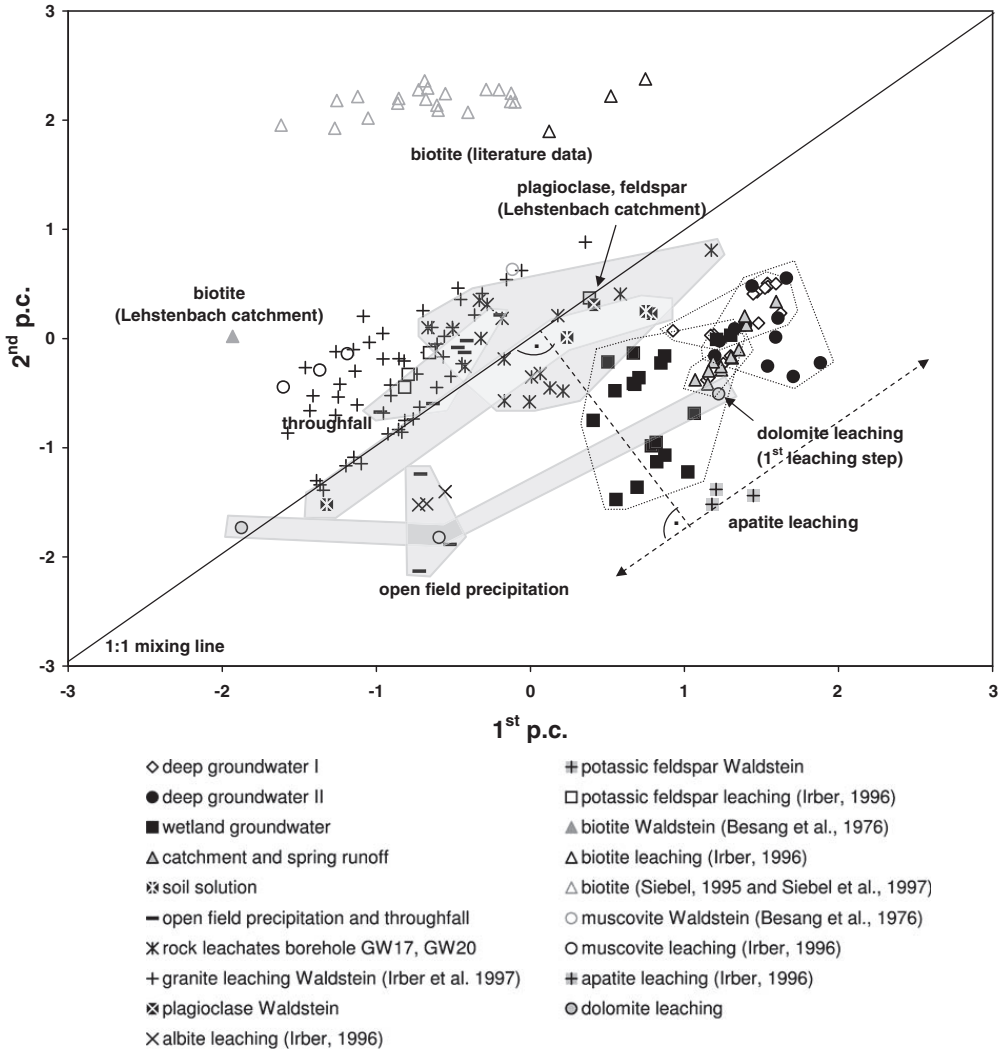

Fig. 8. First principal component (pc) versus second principal component. For better visibility, the data points representing the three groundwater groups, catchment and spring runoff, soil solution, throughfall, open field precipitation and solid rock leachates are underlaid in grey.

tion, the results will be interpreted with respect to the sequence of contribution of single minerals to the base cation release. Biogeochemical processes like plant-uptake, element-cycling and temporary ion-exchange processes are considered to play a negligible role for groundwater of more than 1 m depth.

5.1. Leaching experiments

Bullen and Kendall (1998) and Drever and Clow (1995) point out that laboratory experiments still fail to accurately simulate the effect of long-term weathering under field conditions. Thus, different approaches have been followed in different studies. That has to be taken into account when results from different leaching studies are compared. In this study, deionized water was used. Thus, the actual dissolution kinetics in situ might have been systematically underestimated. In contrast, Clow et al. (1997) used NH_4-acetate for their sequential leaching experiment to extract disseminated calcite. Compared to deionized water, NH_4-acetate is used to quantitatively extract calcite and thus probably overestimates elemental release in situ. Irber et al. (1997) and Harlavan and Erel (2002) used a low pH solution for their leaching experiments. Correspondingly, Blum et al. (2002) investigated dissolution rates of apatite and feldspars at a pH between 2 and 5. In contrast, groundwater samples from the Lehstenbach catchment showed pH values between 4 and 7. More complex dissolution experiments at different pH ranges and using different experimental conditions are described by Guidry and McKenzie (2003), Tang et al. (2003), Valsami-Jones et al. (1998), and Jahnke (1984). Although these experiments tend to provide quantitative information about the dissolution rates of different minerals, Casey et al. (1993) point out that the appropriate level of comparison of field and laboratory weathering is at the scale of reactivity trends and not at that of quantitative similarity in reaction rates.

5.2. Additional element sources

It has to be taken into account, that weathering is not the only source of base cations in the groundwater. Input via atmospheric deposition was determined by the

throughfall samplers. In addition, there are two other sources that need to be discussed.

5.2.1. Liming

During the last decades, the Lehstenbach upslope area was repeatedly limed to counteract the harmful effects of acid deposition on the soils. Liming was performed in the wetlands to avoid enhanced mineralization of the peat. Usually, about 4 t ha^{-1} dolomite were applied during single campaigns. Different parts of the catchment were limed during different campaigns. Assuming one liming campaign per decade, annual Ca input via liming is about 20 times that by deposition (Lischeid et al., 2004b), and about 0.2% of the total Ca pool of the regolith (Besang et al., 1976). Correspondingly, a considerable amount of Sr input has to be taken into account (Clow et al., 1997; Probst et al., 2000).

In subsequent liming campaigns, different materials were used with presumably different $^{87}Sr/^{86}Sr$ ratios. Only those in leachates of the dolomite used during the last campaign could be measured. The values of $0.708051 \pm 6 \times 10^{-7}$–$0.708142 \pm 8 \times 10^{-7}$ correspond well to the data for dolomite given in the literature, ranging between 0.7056 and 0.7095 (Fouke et al., 1996; Sillen et al., 1998; Zachariah et al., 1999; Qing et al., 2001; Drouet et al., 2005).

As only the upslope sites were limed, dolomite could explain the difference in Sr concentration between the wetland and the deep groundwater components. Dolomite would also be in line with the higher Ca/Na ratios of the water samples compared to that of plagioclase (Fig. 6). Numerous studies have focused on the response of soil solution and surface water to liming (e.g. Geary and Driscoll, 1996; Driscoll et al., 1996; Traaen et al., 1997; Alewell et al., 2000; Frank and Stuanes, 2003; Hindar et al., 2003; Dorland et al., 2005). However, the impact of liming on groundwater quality is rarely addressed. Gunn et al. (2001) did not find a clear effect of liming on groundwater quality at a study site at Sudbury, Canada, within the first year. Peters et al. (1999) and Lorz et al. (2003) did not observe any effect of liming on stream water Ca concentration in two Czech shallow soil catchments. They ascribed that to ion exchange processes in the topsoil. Driscoll et al. (1996) argue that dissolution of applied $CaCO_3$ in freely draining upland soils is relatively limited in contrast to wetland soils and thus could have little effect on soil solution chemistry. Correspondingly, in the Lehstenbach catchment, monitoring of groundwater wells and springs downslope of areas that were limed in 1999 did not show any increase of Ca concentration within six years. Accordingly, the high Ca concentrations after drilling in the new groundwater wells can not be explained by liming. Moreover, liming cannot be the reason for the difference of $^{87}Sr/^{86}Sr$ ratios and Ca/Na ratios between the two deep groundwater groups. Thus, it is concluded that liming should not be considered a major Ca source for the groundwater.

5.2.2. Contamination by filter gravel

According to the Sr isotope and base cation ratios, two different groups of deep groundwater wells could be discerned (Figs. 4 and 6). These two groups differ neither with respect to mean gauging depth nor to location within the catchment or to the fraction of unweathered bedrock in the drill cores. However, the deep groundwater wells of the second group were installed later compared to the first group, and were installed in a different manner. Thus, whether this distinction is based on an artefact needs to be checked. The most probable reason for that would be a contaminated filter gravel as has been observed elsewhere (Kloppmann et al., 2001; Malard et al., 2005).

Unfortunately, no samples from the filter gravel were available, and any inferences are based on indirect evidence only. However, there is some evidence that point to filter gravel contamination. First of all, the high Ca concentrations in the groundwater samples observed immediately after installation of the new wells, and the slow decrease thereafter (Fig. 2) are consistent with filter gravel contamination. Moreover, the delayed increase of Ca concentration in well 13a compared to that of well 20a, which is located exactly upstream of the former, can be explained by a contamination plume that has been released by a point source upstream. In fact, the observed time lag corresponds to mean groundwater flow velocity in the catchment. Second, the catchment runoff is located between deep groundwater group I and the wetland groundwater group in the mixing diagrams (Figs. 4 and 6). Thus, it can be argued that the wells of group II are affected by contamination which is restricted to the close proximity of the wells and which does not show up in the stream.

Third, a crude mass balance approach helps to identify the most probable source of the high Ca concentrations in the second deep groundwater group. Filter gravel was installed between 1 and 10 m. Assuming, that the cross-sectional zone of influence is about 1 m^2, accounting for converging groundwater flow lines in the vicinity of the well, considering a mean porosity of 0.1, and a groundwater flux velocity of 5×10^{-6} m s^{-1}, then the volume of affected groundwater of 9 m^3 would be exchanged 160 times/a. The observed maximum increase of Ca concentration at well GW20a by about 20 mg L^{-1} during the first year would then correspond to a release of 2.88 kg Ca.

The total mass of filter gravel per well is about 580 kg. Correspondingly, contamination of the filter gravel with 1.2% $CaCO_3$ would be necessary to release 2.88 kg Ca. That seems to be a plausible amount. The maximum amount of Ca that could be released by apatite weathering is in the same range. According to Richter and Stettner (1979), accessory minerals sum to 0.3% of the bedrock mass. Assuming, that this is entirely due to apatite, and that the diameter of the cross sectional area where weathering was enhanced by drilling is about twice the diameter of the drilling core, and that the density is 2.5 g cm^{-3}, this would correspond to 8.34 kg apatite. Assuming further that the apatite is purely $Ca_5(PO_4)_3(OH)$, this would be equal to 3.33 kg Ca which is in the order of that found in the groundwater. Based on these very optimistic assumptions, the total Ca mass provided by apatite weathering would indeed have been sufficient for explaining the observed increase in Ca concentration in the groundwater at well GW20a in the first year. However, apatite would then have been completely dissolved. Thus, apatite dissolution alone

would have been insufficient to explain the high amounts of Ca released over a period of several years as was observed in the groundwater of the new wells.

According to Fig. 3, deep groundwater wells of the first and second group do not only differ with respect to Ca concentrations, but also with respect to Sr isotope ratios. However, the linear correlation between Ca concentration and Sr isotope ratios in groundwater wells from the affected wells GW11–GW20a is not significant at the $\alpha = 0.1$ level. Thus, it is concluded that Ca concentration data and Sr isotope ratios point to different sources.

5.3. Three different approaches to identify the weathering sequence

Three different approaches were used to identify the sequence of base cation release by different minerals in the Lehstenbach catchment. It was hypothesized that the contribution of different minerals to base cation supply of the groundwater with increasing weathering intensity would be observed by investigating

(1) unweathered rock leachates, deep groundwater and shallow groundwater;
(2) groundwater samples from new groundwater wells, reflecting the initial weathering of the drilled bedrock, and groundwater from wells that were drilled in 1988;
(3) stream water baseflow period, dominated by deep groundwater contribution, and stream water during high flow, being dominated by shallow groundwater.

5.3.1. Rock leachates, deep groundwater and shallow groundwater

Three distinct groups of groundwater wells were identified based on Sr isotope ratios and base cation values: Wetland wells, upslope deep groundwater wells mostly installed in 1988 (deep groundwater group I), and upslope deep groundwater wells installed in 1995 or later (deep groundwater group II). Mean gauging depth does not differ between the latter two groups. In addition, there is no clear depth dependency of isotope ratios or base cation concentration within the single groups. Please compare GW02 and GW04 with the shallow wells in the wetland group (Table1, Figs. 4 and 6), GW03 (top) and GW03 (bottom) in the deep groundwater group I, and GW13a–c and GW20a–c in the deep groundwater group II.

In contrast, the lower Sr isotope ratios and lower cation concentrations in the wetland groundwater are mostly due to a larger contribution of precipitation and throughfall water (Figs. 4 and 6). This is corroborated by the fact that soil solution at the upslope sites GW03a and GW06 exhibited a corresponding shift, compared to the groundwater samples from the same sites. Correspondingly, Aubert et al. (2002) found clear differences between upslope groundwater and saturated zone groundwater in the granitic Strengbach catchment in the Vosges Mountains in France.

However, mixing with precipitation cannot explain the low Sr isotope ratios in the drill core leachates of the wells that were installed in 1995, which are substantially less compared to plagioclase, feldspars or biotite (Fig. 6). It has been argued before that the low Sr isotope ratios in the groundwater of these wells are not correlated with the high Ca concentration released by the filter gravel. Correspondingly, an effect of liming is not very likely. Apatite dissolution would be in line with the low Sr isotope ratios. However, the Ca/Na and Rb/Sr ratios of the rock leachates are opposite to those of apatite (Figs. 4 and 6; Rb/Sr ratios not shown). In contrast, factor values of most of the rock leachates on the two principal components are in the range of those of plagioclase and K-feldspar from the Lehstenbach catchment. On the other hand, some rock leachate samples (GW17 3–4 m and 6–7 m) show higher Sr isotope ratios than those of plagioclase and more similar to those of biotite than to those of feldspars (Figs. 6 and 8). Thus, the rock leachates point to (preferential) cation release from feldspars and biotite dissolution in an initial phase of weathering (Brantley et al., 1998; Stillings et al., 1996; see discussion below).

5.3.2. New groundwater wells and wells drilled in 1988

Groundwater from the new groundwater wells differs from groundwater from the wells drilled in 1988 with respect to their Sr isotope ratios and element ratios (Figs. 4 and 6). As discussed above, this was mainly due to contamination by filter gravel in the new wells. However, due to the lack of correlation between Ca concentrations and $^{87}Sr/^{86}Sr$ ratios in the groundwater of the new wells, the low $^{87}Sr/^{86}Sr$ ratios in the groundwater of the new wells can in part be ascribed to another base cation source than filter gravel contamination. Apatite dissolution and preferential release of non radiogenic Sr from feldspars would be in line with the low Sr isotope ratios (see discussion below). This confirms the conclusion, that apatite and preferential release from feldspars play an important role for the release of base cations in the initial phase of weathering as was deduced from rock leachates.

In contrast, $^{87}Sr/^{86}Sr$ ratios in groundwater from wells drilled in 1988 (deep groundwater group I) are similar to those of plagioclase (Fig. 4). However, Ca/Na ratios of this group are between those of plagioclase and those of biotite and apatite (Fig. 6). Moreover, water samples plot between feldspars and biotite on the one hand and apatite leach samples on the other hand in the PCA (Fig. 8). Thus, it is concluded, that biotite and apatite have to be considered as base cation sources for groundwater from the old wells. In fact, two different element sources like biotite and apatite dissolution could yield a Sr isotope ratio similar to that of plagioclase (Bullen and Kendall, 1998). There is likely a contribution from plagioclase and feldspar to the buffer capacity of groundwater as well, but to an unknown degree.

To summarize, except for biotite, that seems to play an important role for the groundwater in the old wells, no clear differences of base cation sources between the old and the new wells could be observed. Contamination by filter gravel probably masks differences in the weathering degree between the two groups.

5.3.3. Time series of stream water and groundwater solute concentration and isotope ratios

It was assumed that the contribution of precipitation, soil solution and shallow groundwater component should increase during extended high flow periods. In fact, Sr isotope ratios and Sr concentrations of stream water and of groundwater samples at well GW03a and GW04 became more similar to that of rainwater and soil solution from upslope sites during the high water period (Fig. 4). In contrast, temporal variability in well GW06 is almost negligible. This is traced back to the fact that the groundwater level in GW06 was much lower compared to GW03a and GW04. A similar decrease of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in the stream was observed, e.g., by Clow et al. (1997) and by Åberg (1995). Åberg (1995) explained this as the increasing contribution of rainwater to the stream which seems to hold for the Lehstenbach catchment as well.

Throughfall $^{87}Sr/^{86}Sr$ ratios were modified compared to those of open field precipitation (Fig. 6) due to dry deposition on trees and leaching of needles (Graustein and Armstrong, 1983; Gosz and Moore, 1989). The higher values of the second principal component (K, Rb) of throughfall samples compared to open field precipitation can be ascribed to K and Rb leaching from the spruce-needles (Fig. 8). Potassium and Rb show very similar chemical properties and therefore similar chemical behaviour. The temporal variability of the $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in open field precipitation and throughfall is attributed to factors like the meteorological conditions (Graustein and Armstrong, 1983) and thus to variations of atmospheric composition.

To summarize, consistent patterns were found in the time series of Sr isotope ratios and base cation concentration in stream water and groundwater. However, this was mainly due to an increasing fraction of soil water and precipitation during high flow. Correspondingly, these time series could not be used to infer the varying contributions of different minerals that prevail at different stages of granite weathering.

5.4. The weathering sequence

In spite of the restrictions discussed above, the data give some information about the weathering sequence of the Lehstenbach granite, similarly as has been found elsewhere (Bullen and Kendall, 1998; Bullen et al., 1997; Blum and Erel, 1997; Hodson et al., 1996; White et al., 2001). These results are summarized as follows.

5.4.1. Plagioclase and feldspar

Beside quartz, plagioclase and feldspar are the prevailing minerals. In spite of that, these minerals cannot be considered as endmembers due to their low Ca/Na ratio (Fig. 6) and low factor values for the two principal components (Fig. 8). The plagioclase and feldspar sample from the Fichtelgebirge region plot within the range of the Lehstenbach groundwater samples. The calculated saturation indices revealed that all deep groundwater samples are oversaturated with respect to plagioclase and feldspar. Sodium-rich plagioclase was found to be stable in river waters and groundwaters with alkaline pH (pH 7–10) (Gíslason and Arnórsson, 1993). This seems to hold for the waters in the catchment as well (pH 5–7), although the saturation state becomes pH dependent below pH 7.

However, the lower Sr isotope ratios and higher Ca/Na ratios of the deep groundwater group II, i.e. the new wells-group, could in part be attributed to a preferential release of non-radiogenic Sr yielding a Sr isotope ratio lower than that of the bulk mineral in an initial stage of weathering as described for microcline and albite by Brantley et al. (1998). Similar to Sr, high values of Ca and Na can be observed early in dissolution (Stillings et al., 1996). This is corroborated by a lower Sr isotope ratio but a similar Ca/Na ratio of most of the solid rock leachates compared to that of plagioclase and feldspar (Fig. 6).

The mixing of biotite and the dissolution of another base cation source with a low Sr isotope ratio (apatite, preferential release from feldspars, liming) in deep groundwater may result in a $^{87}Sr/^{86}Sr$ ratio near to that of plagioclase and feldspars (deep groundwater group I). Thus, plagioclase and feldspars certainly contribute to the buffer capacity of the groundwater in addition to biotite, apatite and/or liming, although to unknown degrees. However, trace minerals like calcite or apatite can play a major role in the chemical weathering of granitoid rocks despite their minor fraction in the bedrock (White et al., 1999; Aubert et al., 2002; Oliva et al., 2004). This is corroborated by a Ca excess found in many groundwater and surface water samples relative to the plagioclase stoichiometry (e.g. Clow et al., 1997; Blum et al., 1998; White et al., 1999; Probst et al., 2000; Oliva et al., 2004).

5.4.2. Biotite

According to the results, the buffer capacity of the deep groundwater is dominated by biotite weathering. All water samples outside the wetlands were highly undersaturated with respect to biotite. Due to the high K and Rb concentration, all data for biotite samples in the literature exhibited high factor values for the second principal component. Correspondingly, some of the unweathered rock leachates and the deep groundwater samples from the Lehstenbach catchment had high factor values for this component (Fig. 8). This corresponds to the fact that biotite is considered to be easily weathered (Blum and Erel, 1997; Bullen et al., 1997; Hodson et al., 1996). In contrast, Drever and Clow (1995) argue that biotite weathering rates do not exceed those of feldspars due to oxide coatings attached to the minerals.

5.4.3. Apatite

Apatite data in the literature exhibit a high variance of element concentration and Sr isotope ratios that renders a clear interpretation difficult (Bonhomme, 1967; Van Gaans et al., 1995; Sun and Higgins, 1996; Tilton et al., 1997; Charoy, 1999; Sha and Chappell, 1999; Négrel et al., 2001). However, the apatite leachates analysed by Irber (1996) could be regarded as a missing endmember for the deep groundwater samples (Figs. 4, 6 and 8). These samples were taken from granite in the Ore Mountains, but of the same age as the Lehstenbach catchment granite. The low Sr isotope ratio of 0.711416 is comparable with

the value of 0.709 given by Bonhomme (1967) for the Brézouard granite apatite in the Vosges mountains (France) and of 0.70679 by Négrel et al. (2001) for the Monzogranite apatite in the Vienne District (west of the french Massif Central). All these rocks are about the same age between 288 and 315 Ma.

As apatite is non radiogenic (Probst et al., 2000) and has a low $^{87}Sr/^{86}Sr$ ratio, apatite dissolution would be in line with the low Sr isotope ratios of deep groundwater II samples and the second base cation source in addition to biotite of deep groundwater I samples. This hypothesis would be consistent with the Rb/Sr ratios of the deep groundwater samples that are very close to those of apatite (data not shown) and the higher Ca/Na ratios of nearly all water samples compared to those of plagioclase (Fig. 6). Moreover, deep groundwater samples had high factor values of the first principal component (Fig. 8), indicating an important influence of a Ca- and Sr-rich source. Last but not least, the groundwater samples were highly undersaturated with respect to apatite.

According to Irber et al. (1997), apatite has to be considered as a major host of Sr in the Lehstenbach granite. They found between 1000 ppm for early-formed apatites to 10,000 ppm in late formed apatite grains. Based on acid leaching experiments, several authors have found apatite to be an easily soluble trace mineral releasing considerable amounts of Sr (Irber et al., 1997; Blum et al., 2002; Harlavan and Erel, 2002). Oliva et al. (2004) concluded that more than 80% of the Ca export from the watershed can be attributed to the weathering of trace minerals (epidote, prehnite, apatite and bytownite). However, the dissolution rate of apatite is pH dependent and is at its minimum at circumneutral pH, corresponding to the range of pH 5–7 in the waters in the Lehstenbach catchment (Wu and Forsling, 1995; Valsami-Jones et al., 1998; Guidry and McKenzie, 2003). Although the dissolution rate of apatite depends also on factors such as the distance from equilibrium (Guidry and McKenzie, 2003), the carbonate content (Jahnke, 1984) and the presence of weak acids (Tang et al., 2003), the dissolution rate of apatite is always higher than those of silicate minerals (feldspars, biotite), but lower than those of carbonates (calcite, dolomite).

Based on Sr isotope and element ratios, the influence of apatite could not be distinguished from dolomite as a base cation source (Figs. 4 and 6). Only the greater distance of apatite compared to that of dolomite from the 1:1 mixing line in the PCA plot and the considerations given above with respect to the role of liming for groundwater point to apatite rather then to dolomite as the missing endmember.

To summarize, apatite seems to play a role as a base cation source in the initial stage of weathering. However, its influence is apparently obscured due to contamination by filter gravel.

5.4.4. Calcite

Several authors have found that disseminated calcite, a very soluble trace mineral (e.g. Hodson et al., 1996), can have an important influence on the chemical composition of surface waters and groundwaters in crystalline catchments and can explain excess Ca (Clow et al., 1997; Blum et al., 1998; White et al., 1999; Jacobson and Blum, 2000; Négrel et al., 2003). Clow et al. (1997) showed that weathering of calcite, present in trace amounts in silicate bedrock (Loch Vale, Colorado) can account for between 43 and 59% of the total Ca flux in stream water. Blum et al. (1998) found that the cation and HCO_3 flux in a predominantly silicate watershed within the High Himalayan Crystalline Series is predominantly derived from dissolution of a small amount of calcite (~1%).

The Sr isotope ratios of the unweathered rock leachates determined in the study varied over a wide range independent of the number of leaching steps (Fig. 6). Thus, no single element source could be identified. Moreover, Sr isotope ratios for trace calcite in granite vary between 0.706 (Blomqvist et al., 2000) and 1.06962 (Clauer et al., 1989). However, in the study the Ca/Na ratios of the leachates were lower compared to the groundwater samples (Fig. 6), and the leachates plot in the opposite direction in the principal component diagrams, compared to calcite and apatite (Fig. 8). Furthermore, Besang et al. (1976) and Stettner (1964) do not mention calcite as an accessory mineral in the granite bedrock in contrast to apatite. Thus, it is concluded that the role of calcite is negligible in the Lehstenbach catchment.

6. Conclusions

The role of different minerals in base cation release, thus increasing the buffering capacity of groundwater against acid deposition, is controversially discussed in the literature. The $^{87}Sr/^{86}Sr$ ratios and base cation concentration in whole rock leachates, mineral separates, precipitation, soil solution, groundwater and stream water samples in the Lehstenbach catchment (Germany) were investigated to identify the weathering sequence of the granite bedrock.

Feldspar weathering contributes to base cation release, but these minerals cannot be regarded as endmembers of the mixing diagram. Instead, biotite weathering played an important role for base cation release. In addition, there was some evidence that apatite played an important role in the initial stage of weathering. There was no clear evidence for a contribution from calcite. Correspondingly, base cation input by atmospheric deposition and liming had only minor effects on groundwater buffer capacity.

The extensive study revealed some ambiguities and coincidences that had to be investigated carefully. In contrast to prior assumptions, the observed decrease of the Sr isotope ratios in the stream during discharge peaks did not reflect the contribution of a different weathering system in the upper aquifer layers, but was due to the increased contribution of precipitation and soil water. The exceptionally high release of Ca in some wells shortly after installation was in the first place due to contaminated filter gravel. In contrast, the observed decrease of the Sr isotope ratios in these wells was consistent with that of the drilling core leachates, pointing to preferential cation release by feldspars in an initial phase of weathering. Although the extensive data set yielded a puzzling picture at the first sight, it was concluded that this critical mass of data was necessary to prevent premature inferences.

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Study 5

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Acidification processes and soil leaching influenced by agricultural practices revealed by strontium isotopic ratios

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Abstract

In natural river systems, the chemical and isotopic composition of stream- and ground waters are mainly controlled by the geology and water–rock interactions. The leaching of major cations from soils has been recognized as a possible consequence of acidic deposition from atmosphere for over 30 years. Moreover, in agricultural areas, the application of physiological acid fertilizers and nitrogen fertilizers in the ammonia form may enhance the cation leaching through the soil profile into ground- and surface waters. This origin of leached cations has been studied on two small and adjacent agricultural catchments in Brittany, western France. The study catchments are drained by two first-order streams, and mainly covered with cambisoils, issued from the alteration and weathering of a granodiorite basement. Precipitations, soil water- and NH_4 acetate-leachates, separated minerals, and stream waters have been investigated. Chemical element ratios, such as Ba/Sr, Na/Sr and Ca/Sr ratios, as well as Sr isotopic ratios are used to constrain the relative contribution from potential sources of stream water elements.

Based on Sr isotopic ratio and element concentration, soil water- and NH_4 acetate leaching indicates (1) a dominant manure/slurry contribution in the top soil, representing a cation concentrated pool, with low $^{87}Sr/^{86}Sr$ ratios; (2) in subsoils, mineral dissolution is enhanced by fertilizer application, becoming the unique source of cations in the saprolite. The relatively high weathering rates encountered implies significant sources of cations which are not accessory minerals, but rather plagioclase and biotite dissolution.

Stream water has a very different isotopic and chemical composition compared to soil water leaching suggesting that stream water chemistry is dominated by elements issued from mineral and rock weathering. Agriculture, by applications of chemical and organic fertilizers, can influence the export of major base cations, such as Na^+. Plagioclase dissolution, rather than anthropogenically controlled soil water, seems to be the dominant source of Na^+ in streams. However, Ca^{2+} in streams is mostly derived from slurries and manures deposited on top soils, and transferred into the soil ion-exchange pool and stream waters. Less than 10% of Na^+, 5–40% of Sr^{2+} and 20–100% of Ca^{2+} found in streams can be directly derived from the application of organic fertilizers.

1. INTRODUCTION

Acid deposition has been an important and increasing cause of soil acidification in Europe since the industrial revolution and, recently with the development of intensive

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livestock production and the resultant large emissions of ammonia. The acidification induced by acidic compounds produced by industrial activities has been widely investigated on natural and forested silicate catchments (Armbruster et al., 2003; Fernandez, 1985; Fernandez et al., 2003; Likens et al., 1998; Stoddard et al., 1999). Ammonium-based fertilizers have dramatic consequences on metal mobilization and plant uptake (Goulding and Blake, 1998) and represent the single most significant cause of soil acidification on most agricultural land (Ganev, 1992; Graham et al., 2002). The acidification phenomenon is not only localized on the topsoil, but propagates into the subsoil, which becomes more acid than the topsoil (Goulding and Annis, 1998). Soil acidification causes cation depletion and possible accelerated leaching of base cations from soils, thus increasing major base-cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) concentrations and fluxes in soil solutions and surface waters (Driscoll et al., 2001; Johnson et al., 1991). This is attributable to ion-exchange reactions in the soil, which result in the loss of mineral cations from the soil by leaching while H^{+} accumulates in the exchange complex (Barak et al., 1997; Graham et al., 2002; Sverdrup et al., 1994).

In silicate bedrock, the major sources of base cations and the most abundant minerals are plagioclase, potassic feldspar, biotite and muscovite (Goulding and Annis, 1998; Lasaga et al., 1994; Probst et al., 2000; Sverdrup and Warfvinge, 1995). Trace minerals such as apatite and calcite, have been identified as potential major sources of Ca in ground- and stream waters, in addition to Ca–plagioclase weathering (Aubert et al., 2002; Blum et al., 2002; Clow et al., 1997; Fernandez et al., 2003; Oliva et al., 2004; Sverdrup and Warfvinge, 1995; White et al., 1999). In soil chemistry, the major cation release, the Al production rate and the neutralization of acidity, all depend on the chemical weathering of soil minerals (Sverdrup, 1996). The soil zone, where the weathering is intense, has traditionally been considered as dominant in the weathering process and the export of solutes from catchments (Shand et al., 2007). But the export of solutes may be derived from less intense weathering of large volumes of rocks in the subsurface environment below the soil. The respective contribution of these two main zones is variable and is not clearly defined. However, some authors do not consider that soil acidification has an impact on the mineral weathering rates (Fernandez et al., 2003; Gbondo-Tugbawa and Driscoll, 2003; Sverdrup et al., 1995). The acidification process is rather associated with leaching of soil base cations from the exchange complex and the mobilization of toxic forms of aluminium, leading to a decrease of the soil base saturation (Dahlgren et al., 1990; Wright et al., 1988).

The strontium isotopic composition ($^{87}Sr/^{86}Sr$) has been extensively used in order to (i) determine the sources of Ca in stream- and ground waters in weathered environments (i.e. (Åberg and Jacks, 1987; Clow et al., 1997; Dupré et al., 1996; Gaillardet et al., 2003; Miller et al., 1993) and (ii) to investigate water–rock interactions during weathering processes and solute transport (i.e. (Bullen et al., 1996; Collerson et al., 1988; Franklyn et al., 1991; Johnson and Depaolo, 1997; Katz and Bullen, 1996; Neumann and Dreiss, 1995). More recently, several studies have shown contamination of stream- and ground waters by agricultural activities based on the complex chemical and isotopic signatures of waters, soils, rocks and fertilizers (Böhlke and Horan, 2000; Nakano et al., 2005; Vitòria et al., 2004; Widory et al., 2004). Sr isotopic composition and concentration in runoff, soils, waters and biomass are primarily dependent on mixing between atmospheric inputs and mineral weathering sources, but also human-influenced sources, such as fertilizers. Strontium of all these sources may be included in the cation exchange pool and further interact with catchment soil solutions (Åberg et al., 1989; Bullen et al., 1996; Katz and Bullen, 1996). The $^{87}Sr/^{86}Sr$ ratio in waters will therefore be a function of the weatherable and exchangeable Sr signatures as well as hydrological processes (Åberg et al., 1989). It may be a powerful tool to discriminate between mineral and agricultural sources in catchments influenced by anthropogenic activities.

Brittany, western France, is an interesting place for studying the impact of agriculture on soil and water chemistry, quality and stability, because of the development of intensive agriculture since the late 1960's. This study has been conducted on a field area that has been previously studied in order to determine the variability of the transfer of nitrates from soil to stream waters through ground waters and to determine the respective hydrobiogeochemical compartments of the catchment (Legout et al., 2007, 2005; Martin et al., 2004; Ruiz et al., 2002a,b). A previous study focused on the determination of chemical weathering rates based on atmospheric inputs, mineral weathering and agricultural contributions (Pierson-Wickmann et al., in press). It indicated a direct relationship between high agricultural pressure and enhanced chemical weathering rates, which were much higher than in any other small granitic catchments. In this study, the Sr isotopic composition and major cation concentrations have been determined in the same two small granitic catchments, Kerbernez and Kerrien, located in western Brittany in order to determine the mineralogical sources of the high cation loads, induced by agricultural activities.

2. GEOLOGICAL SETTING AND HYDROLOGICAL CONTEXT

The Kerbernez and Kerrien catchments are located in south-western Brittany, France (47°57′ N–4°8′ W), roughly 550 km west of Paris (Fig. 1). Kerrien (0.095 km^2) and Kerbernez (0.120 km^2) are two adjacent first-order catchments, which consequently share the same lithological and climatic characteristics. The different catchment streams join a river 10 km before it flows into the Atlantic Ocean. The climate is oceanic. Mean annual precipitation and potential evapo-transpiration (calculated on the last decade) are 1161 and 616 mm, respectively (Legout et al., 2005; Ruiz et al., 2002a). The rainiest seasons are autumn and winter. Mean monthly temperatures reach a minimum in January (6.1 °C) and a maximum in July (17.6 °C) (Ruiz et al., 2002a).

The bedrock belongs to the Paleozoic leucogranodiorite of Plomelin (Béchennec et al., 1999).The granite is fractured and fissured, and is overlaid by weathered material, with a

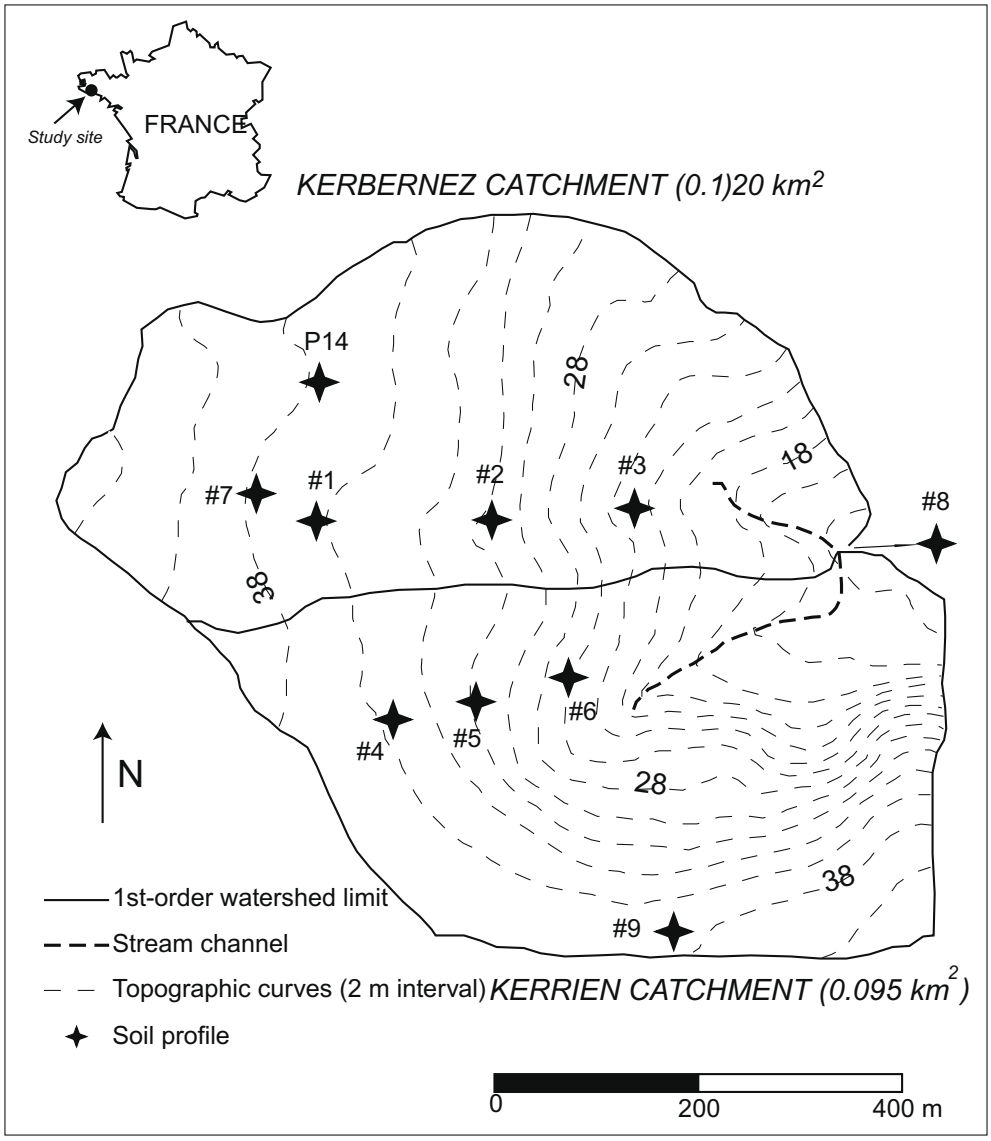

Fig. 1. Location map of Kerbernez and Kerrien catchments (Brittany, northwestern France), showing the different sampling sites (soils and streams). Stars represent soil profiles.

mean thickness of about 20 m and is slightly thicker in Kerbernez than in Kerrien (Legchenko et al., 2004). The principal minerals in the granodiorite are quartz, plagioclase (albite-oligoclase), K-Feldspar, muscovite and biotite. Secondary minerals, such as clays (i.e. kaolinite and illite) are also present in the granitic arena. After Béchennec et al. (1999), some accessory minerals include apatite, garnet and zircon. However, despite previous apatite observation (Béchennec et al., 1999), no apatite has been observed in our rock and soil samples.

Soils are mainly brown sandy loam (distric cambisol, FAO classification) developed on a granitic arena. Soil profiles were dug down to C or B/C horizon, finding the weathered granite (C-horizon) between 0.7 and 1.2 m below the soil surface (Legout et al., 2005). The C-contains sand (63%), silt (26%) and clay particles (11%). The B-horizon, a cambic horizon (BW), between 40 and 65 cm depth, displays low organic carbon content (0.5 wt% C) and a higher content of silt particles (~64%) relative to sand (19%) and clays (17%). The upper horizons from 10 to 40 cm depth, corresponding to mineral horizons altered by human-related activities (Ap), are formed by micaceous sand and silt particles and display a higher organic carbon content (2.8 wt% C). The soil bulk density ranges from 1.3–1.5 g cm^{-3} (A and B horizons) to 1.7 g cm^{-3} (C-horizon). Soils are well drained except in the relatively narrow bottomlands where hydromorphic soils are found. Land use is mainly agricultural (77%). Most arable fields (43% of cultivated surface) grow maize and cereals alternately. They are farmed intensively, including importation of pig slurry and cattle manure: an average of 1300 kg/ha of ammonitrates, 40 m^3/ha of pig slurries and 20 kg/ha of manures are applied over a 10 years period (Appendix A). A large part of the grasslands (40% of the cultivated surface) are

grazed intensively by dairy cows (Ruiz et al., 2002a). Lime (CaOMg and local organogenic calcareous sands called Trez) was applied in 2002 and 2005.

An automatic weather station, located 500 m away from the catchments, recorded hourly rainfall and the different parameters required to calculate potential evapo-transpiration by the Penman formula. Catchment outlets were equipped with V-notch gauging stations for weekly discharge measurements. The monitoring period (studied in this paper) comprised four hydrological years, from 01/2001 to 12/2004, including two very contrasting years (2000–2001 and 2001–2002). The first year (from October 2000 to September 2001) was very wet, with a total precipitation of 1760 mm and a potential evapo-transpiration of 690 mm. The second year (from October 2001 to September 2002) was much drier, with a total precipitation of 986 mm and a potential evapo-transpiration of 697 mm (Martin et al., 2004). The catchments are characterized by the presence of shallow ground water developed perennially in the weathered granitic material, with the water table depth ranging from 2 to 8 m below the soil surface throughout the hydrological cycle.

3. SAMPLING AND ANALYTICAL PROCEDURES

3.1. Sampling and analyses

Stream- and rain water samples were collected monthly for the two first years, and then every 3 months from January 2001 to December 2004. Water samples were filtered in the field with 0.20 μm nylon Millipore filters and then stored in HNO_3 acidified and non-acidified vials, for cation and anion analyses, respectively, in the dark at less than 4 °C before analysis. All the analyses have been carried out in the Caren-Geosciences analytical and isotopic laboratories. Major and trace cation concentrations were determined using an Agilent Technologies™ HP4500 ICP-MS instrument (Bouhnik-Le Coz et al., 2001; Yeghicheyan et al., 2001). Experimental protocol of sampling, storage, and analysis has been previously described in Dia et al. (2000). Typical uncertainties including all error sources are <5% for all trace elements, whereas for major anions, the uncertainty lies between 2 and 5%, depending on the concentration levels. Dissolved organic carbon (DOC) concentrations were determined using a Shimadzu 5000 TOC analyzer with an accuracy estimated at ±5%.

Biotite, muscovite, plagioclase and K-Feldspar have been separated from the Plomelin leucogranodiorite using dense liquids and a Frantz isodynamic magnetic separator, and by handpicking under the binocular microscope. A bulk digestion, using HF and HNO_3, has been performed on each mineral fraction in order to determine their geochemical composition. The international standards SLRS-4, and CRPG Biotite Mica-Fe standard, ANRT K-Feldspar FK-N (Govindaraju, 1984, 1995) were used to check the validity and reproducibility of the results.

Soil samples were collected upland to downland in both Kerrien and Kerbernez catchments (Fig. 1). The soils were air-dried and sieved through a 2-mm sieve. Soil pH was measured, using 10 g of soil, after extraction in 20 mL of 0.01 M $CaCl_2$ (pH_{Ca}) by shaking for 30 min. Some soils were analyzed by bulk digestion, NH_4 acetate leaching and water leaching in order to determine the whole pool of cations in soils, the cations available for plants related to ion-exchange complex of the soil (NH_4 acetate leaching, NH_4Ac), and the cations leachable with water flowing through the soil, respectively. The maximum depth of soil samples in the recharge zone is 70 and 110 cm for Kerrien (#9) and Kerbernez (#7), respectively, corresponding to the C-horizon depth. Downland soils (#8) have been sampled at 20, 60, 90 and 120 cm depth.

The NH_4 acetate leaching procedure (NH_4Ac-leaching) consists of a mixing of 10 g of soil sample 100 mL of 1 M NH_4 acetate (pH = 7), then shaken for 30 min and centrifuged at 2900 rpm. The supernatant was filtered at 0.2 μm and then dried. The whole procedure was repeated twice, adding 40 mL NH_4 acetate each time. For water leaching procedure (H_2O-leaching), 10 g of soil sample were leached with 50 mL of deionized water (DI-H_2O), shaken for 20 h and then centrifuged at 2500 rpm. The supernatant solution has been filtered at 0.2 μm, and then acidified with HNO_3. All the final solutions were then analyzed by ICP-MS.

The Sr isotopic composition has been determined on stream waters, soil H_2O- and NH_4Ac-leaches of soils, bulk digest separated minerals and bulk digest soils. The solid material or solution was mineralized with an ultrapure HNO_3–HF mixture and HCl in Teflon vials, until the solution was perfectly clean. Strontium was isolated from the residue using a cation exchange column Bio-Rad Dowex® AG50-WX8, 200–400 mesh, resins for soil leachates and separated minerals, or Sr-SPEC resin (Eichrom® Industries) for rain and stream water samples, and 2 M HCl as the eluant. Strontium isotope ratios were measured using a Finnigan® MAT 262 thermal ionization mass spectrometer fitted with multicollector array consisting of five Faraday cups. Corrections for mass fractionation were made by normalizing $^{86}Sr/^{88}Sr$ to 0.1194. Standard reference material NBS 987 run over the period of analyses gave an average $^{87}Sr/^{86}Sr$ ratio of 0.710258 ± 0.00008 (2σ standard deviations, $n = 15$).

3.2. Calculations

The relative contribution of Sr from soil mineral weathering and fertilizers to waters is calculated using two mass balance equations, that must be satisfied (Eqs. (1) and (2)).

$$[Sr]_M = f \cdot [Sr]_A + (1 - f) \cdot [Sr]_B \quad (1)$$

$$[Sr]_M \cdot (^{87}Sr/^{86}Sr)_M = f \cdot [Sr]_A \cdot (^{87}Sr/^{86}Sr)_A + (1 - f) \cdot [Sr]_B \cdot (^{87}Sr/^{86}Sr)_B \quad (2)$$

where [Sr] and $^{87}Sr/^{86}Sr$ represent the concentration of Sr and Sr isotopic composition, respectively, in each end-member and the mixture. A and B refer to two end-members, being separated minerals or animal manures and M refers to the 'water' mixture component, being waters, H_2O-leachates or NH_4Ac-leachates, and f represents the relative contribution of end-member A.

The different curves are calculated for the provisional weathering of end-members as well as for a range of $^{87}Sr/^{86}Sr$

ratios of soil leachates. On this diagram, various mixtures of two end-members define a hyperbola. The curvature of the mixing lines depends on the differences in Sr isotopic and Ca/Sr ratios of the end-members.

4. RESULTS

4.1. Solid phases: Soil profiles and separated minerals

Table 1 summarizes geochemical data obtained on bulk digestion of separated minerals from Plomelin leucogranodiorite, soil profile (P14) and manures. The H_2O-leaching and NH_4Ac-leaching are presented in Tables 2 and 3 for soil profiles. The combined information provided by the chemical and isotopic data, as well as a comparison with likely source rocks and separated minerals, allows the relative effects of alteration to be constrained.

4.1.1. Separated minerals

The separated minerals from the Plomelin granodiorite (Table 1) present different Sr isotopic ratios, ranging from 0.708 to 0.727 for most minerals and 0.999 for muscovite. The relatively low $^{87}Sr/^{86}Sr$ ratio of the Na–plagioclase is consistent with the relatively low Rb content (17 ppm). However, because of the difficulty of collecting enough material, the Sr isotopic composition of the biotite was not determined, but is presumably much more radiogenic than any other minerals, even muscovite, because of its high K concentration. For the following discussion, the $^{87}Sr/^{86}Sr$ ratio of the biotite is estimated at 3.21, assuming that the minerals are contemporaneous and considering the Sr concentrations of separated minerals and their $^{87}Sr/^{86}Sr$ ratios and the biotite Sr concentrations (plagioclase, K-feldspar and muscovite correlation presents a R^2 coefficient of 0.999). The $^{87}Sr/^{86}Sr$ of plagioclase and K-Feldspar bracket that of stream waters (Tables 4 and 5) and most of soil horizons (Tables 1–3), with a value of 0.7084 for the Na–plagioclase and 0.7186 for the K-feldspar.

4.1.2. Soil profiles

4.1.2.1. Bulk digest soils. Taking into account the pH_{Ca} in all samples (Table 3), Kerbernez soils are considered as strongly acid soils, while Kerrien soils are slightly acid soils. Variations of geochemical parameters with soil depth are shown in Fig. 2, summarizing the H_2O-leaching and bulk digest analyses.

In bulk digest soils (Table 1), the concentrations of Sr, Rb, Na, Ca, Mg and K remain fairly constant in the three upper horizons, between 10 and 50 cm. However, in the two deeper horizons (between 75 and 105 cm), these concentrations increase by 30–100%, indicating a more significant pool of mineral cations in the deeper less weathered soil. The higher K concentrations in the bulk digest of the deeper horizons suggest a remaining source of K in these horizons. However, Ba does not display any variation in concentration with increasing depth in the whole soil profile as well as Ca/Sr ratio which slightly varies from 34 to 44. The bulk Sr isotopic composition is relatively radiogenic, ranging from 0.72351 to 0.72746.

In order to better determine the influence of K-host minerals versus the biotite or muscovite high $^{87}Sr/^{86}Sr$ minerals, the $^{87}Sr/^{86}Sr$ versus the reciprocal Sr concentration is plotted in Fig. 3. A significant correlation ($R^2 = 0.68$ for all bulk digest soils analyzed; $R^2 = 0.98$ for all soils except the alterite at 105 cm depth) is produced for the bulk digest soils, indicating a mixture between two end-members. One of the end-members can be interpreted as including K-feldspar since it is almost directly included in the correlation curve (Fig. 4). The other end-member is unknown. It could correspond to another mixed end-member between a highly radiogenic biotite (~24%) and hog manure (~76%) (Table 6).

4.1.2.2. Water soluble cations in soils. For the soil H_2O-leachates (Table 2, Fig. 2), the different cation concentrations and Sr isotopic composition are more variable with soil depth than for bulk digest soils. Sr and Ca concentrations display an obvious monotonous, decrease with increasing soil depth. This decrease in Sr and Ca concentrations does not mimic that of bulk digest soil, with a Ca/Sr

Table 1
Bulk digestion of soil, separated minerals and manures: Major and trace element concentrations (mg/kg), Sr isotopic composition, and element ratios.

	Sample	Depth (cm)	Na	Ca	Mg	K	Ba	Fe	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	$^{87}Sr/^{86}Sr$
Mineral	Muscovite	–	4733	35	5144	n.d.	364	11747	19.4	442	22.7	18.7	1.8	0.01	0.98892
	Biotite	–	652	2124	47422	87327	828	20240	2.2	1036	463	370	949	3.26	n.d.
	K-feldspar	–	29741	7032	96	n.d.	1162	1084	324	279	0.9	3.6	21.6	0.24	0.71864
	Plagioclase	–	89763	33600	251	5514	70	4873	489	17.1	0.03	0.14	68.7	0.37	0.70845
Bulk digest soil	P14	10	12027	4356	2503	27360	342	19705	101	173	1.7	3.4	43.0	0.36	0.72592
		20	11455	3698	2369	28797	358	17046	99	180	1.8	3.6	37.2	0.32	0.72717
		50	11662	3230	2751	26905	340	19932	95	171	1.8	3.6	33.9	0.28	0.72746
		75	16955	4856	4867	35568	355	30043	128	199	1.5	2.8	37.8	0.29	0.72351
		105	20772	6385	5001	39110	360	21113	144	220	1.5	2.5	44.4	0.31	0.72611
Manure	S4LB a	–	2724	42584	11271	12164	39.6	2340	63.6	10.0	0.2	0.6	670	0.001	0.70939
	S4LB b	–	2786.	43022	11519	12359	39.3	2362	64.0	10.2	0.2	0.6	672	0.001	0.70939
	S1LB	–	3531	35884	14206	15156	35.8	2346	73.6	13.1	0.2	0.5	488	0.001	0.70962

n.d.: not determined. Concentrations determined on dry matter.

Table 2
Major and trace element concentrations (μg/g), Sr isotopic composition, and element ratios of soil H_2O-leachates of Kerrien and Kerbernez catchment soils.

Catchment	Horizon	Soil depth (cm)	Na	Ca	Mg	K	Ba	Fe	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	$^{87}Sr/^{86}Sr$
Kerrien Soil	OA	20	2936	6756	943	4061	3.4	882	36.4	8.4	0.2	0.1	186	2.30	0.70963
#9	A	60	3799	4035	1063	3576	17.1	6470	27.8	21.2	0.8	0.6	145	1.06	0.71333
	B	70	3888	1909	310	2465	5.0	1250	21.2	8.5	0.4	0.2	90	0.49	0.71181
Kerbernez	OA	20	2183	5382	1252	7428	5.7	2125	22.1	12.8	0.6	0.3	243	2.46	0.71022
Soil #7	A	70	1453	2425	661	6342	1.9	344	9.8	5.2	0.5	0.2	248	1.67	0.71047
	B	110	1544	1002	995	8447	20.4	7471	7.4	22.0	3.0	2.8	135	0.65	0.71841
Soil #8	OA	20	2897	7274	4040	13075	123.5	32771	49.4	135.2	2.7	2.5	147	2.51	0.72213
	A	60	2573	3787	819	1849	12.1	2266	18.2	9.7	0.5	0.7	208	1.47	0.71254
	B	90	3883	2260	767	291	2.8	415	14.0	1.4	0.1	0.2	162	0.58	0.71160
	C	120	2615	201	176	1431	6.4	477	2.4	4.7	2.0	2.7	85	0.08	0.72615
Soil P14	OA	10	2673	4805	2160	19158	17.3	8423	26.8	33.6	1.2	0.6	179	1.80	0.71181
	A	20	2954	6710	2495	18313	27.4	12409	37.4	47.3	1.2	0.7	179	2.27	0.71214
	AB	50	2375	3843	1841	9835	24.8	16363	25.4	41.7	1.6	1.0	151	1.62	0.71391
	B	75	1560	1702	513	6024	4.1	2248	12.1	9.9	0.8	0.3	141	1.09	0.70949
	C	105	5293	313	258	6075	4.9	1472	3.3	12.2	3.7	1.4	95	0.06	0.72981

ratio much higher and more variable in H_2O-leachates, ranging from 85 to 248. The high Ca/Sr ratio in H_2O-leachates relative to bulk digest soils is mostly explained by a higher Sr loss than Ca loss, varying with depth. Indeed, the upper horizons release much more Sr than the deeper and less altered horizons (C-horizon or granitic arena), by a factor 2–20. A similar behaviour is observed for Ca, with a larger release factor range from 4 to 36 which explains the very high Ca/Sr in the top soil. In general, the higher cation losses are encountered in the soil sampled at the catchment outlet (#8). Potassium is the main cation released from soil during H_2O-leaching, representing 30–70% of the cations. However, K decreases dramatically in the A and B horizons, becoming unchanged in the deeper horizons, under the alteration front.

In general, the solubility and dissolution rate of plagioclase makes it a major contributor of Na^+ and a major source of Ca^{2+} ions to weathering solutions. It induces a Ca/Na ratio close to that of congruent dissolution of plagioclase in soil solutions and river waters. The Ca/Na ratio in H_2O-leachates and stream waters of both Kerbernez and Kerrien is larger than the ratio in the plagioclase, indicating either the presence of an additional source of Ca^{2+} or a sink of Na^+. The progressive decrease with depth in Sr^{2+} and Ca^{2+} contents in H_2O-leaching experiments (Fig. 2) suggests a more significant labile stock of Ca^{2+} and Sr^{2+} in the surface soil horizons.

The variation of $^{87}Sr/^{86}Sr$ ratios in leachates is neither monotonous, nor correlated to Sr concentration decrease with increasing soil depth. In the upper three horizons

Table 3
Major and trace element concentrations (μg/L), pH_{Ca}, Sr isotopic composition, and element ratios of NH_4Ac-leaching solution of Kerrien and Kerbernez catchments.

Catchment	Horizon	pH_{Ca}	Na	Ca	Mg	K	Ba	Sr	Rb	Rb/Sr	Ba/Sr	Ca/Sr	Ca/Na	$^{87}Sr/^{86}Sr$
Kerbernez	#1 – O	4.77	14.9	1000	110.5	393	4.4	6.0	1.3	0.21	0.73	166	67.2	0.70936
	#1 – AO	4.88	12.4	442	59.7	365	2.3	2.4	1.1	0.45	0.97	1845	35.5	0.70943
	#1 –A	4.92	13.7	408	52.8	406	2.4	2.1	1.1	0.52	1.11	190	29.9	0.70924
	#2 – O	4.39	18.3	675	79.6	311	3.3	4.2	1.3	0.31	0.78	161	36.9	0.70929
	#2 – AO	4.33	13.9	501	71.8	197	2.5	2.9	1.2	0.40	0.87	172	36.0	0.70929
	#2 –A	4.25	11.9	178	33.3	149	1.4	0.9	0.9	0.96	1.46	188	14.9	0.70952
	#3 – O	4.49	20.3	845	58.6	207	4.7	5.0	1.2	0.23	0.94	168	41.6	0.70936
	#3 –A	4.77	18.2	519	40.5	146	4.5	3.4	0.9	0.25	1.29	150	28.5	0.70938
Kerrien	#4 – O	5.37	28.4	2000	134.7	320	3.6	13.7	1.4	0.10	0.26	146	70.5	0.70925
	#4 – AO	5.24	26.1	1102	89.9	178	3.3	7.3	1.1	0.15	0.45	151	42.1	0.70922
	#4 –A	5.26	21.3	556	54.5	199	3.7	4.6	0.8	0.18	0.79	119	26.1	0.70947
	#5 – O	5.21	28.0	1443	59.0	207	4.9	9.9	1.2	0.12	0.49	145	51.6	0.70944
	#5 – AO	4.91	23.2	840	38.6	109	4.4	5.9	1.2	0.21	0.74	141	36.2	0.70916
	#5 –A	5.10	13.7	371	27.3	103	4.6	3.0	1.0	0.34	1.53	123	27.2	0.70943
	#6 – O	6.51	19.3	2579	132.4	173	5.0	18.0	0.9	0.05	0.28	143	133.3	0.70921
	#6 – AO	5.99	20.7	1672	110.6	191	3.1	13.0	1.3	0.10	0.24	128	80.8	0.70936
	#6 – A	6.27	18.5	826	54.6	186	3.6	9.6	1.2	0.13	0.37	86	44.5	0.70918

Table 4
Major and trace element concentrations (μg/L), Sr isotopic composition, and element ratios of stream water at the Kerbernez catchment outlet.

date	pH	Na	Ca	Mg	K	Ba	Sr	Rb	DOC (mg/L)	Rb/Sr	Ba/Sr	Ca/Sr	Ba/Ca	Ca/Na	$^{87}Sr/^{86}Sr$
17/01/2001	6.5	25620	16570	10440	4290	24.1	161.5	4.8	2.29	0.030	0.149	102.6	0.0015	0.647	
14/02/2001	5.89	24620	15520	10450	4005	24.1	162.6	4.7	1.90	0.029	0.148	95.4	0.0016	0.630	
14/03/2001	6.32	24853	16528	11278	3825	24.9	163.6	4.6	4.93	0.028	0.152	101.0	0.0015	0.665	
11/04/2001	5.88	23190	15090	10440	3899	24.0	165.8	4.6	2.85	0.028	0.145	91.0	0.0016	0.651	0.71104
09/05/2001	5.94	22140	13990	10320	3359	26.2	165.8	4.4	1.32	0.026	0.158	84.4	0.0019	0.632	
06/06/2001	6.02	24350	13970	10250	4326	27.4	164.2	5.4	2.14	0.033	0.167	85.1	0.0020	0.574	0.71113
04/07/2001	6.2	25400	18250	12380	4201	28.4	171.3	5.2	2.27	0.031	0.166	106.5	0.0016	0.719	
01/08/2001	6.09	25050	16420	10090	4010	24.5	161.3	5.0		0.031	0.152	101.8	0.0015	0.655	
29/08/2001		23950	16770	10310	4645	23.6	163.1	5.7	2.91	0.035	0.145	102.8	0.0014	0.700	
26/09/2001	6.79	24180	15090	11460	4602	24.3	168.4	5.3	1.87	0.031	0.144	89.6	0.0016	0.624	
16/10/2001	6.59	25310	15940	11460	4329	29.8	177.5	5.1	1.27	0.029	0.168	89.8	0.0019	0.630	
14/11/2001	5.94	24310	14930	10810	4158	28.5	164.1	4.8	1.06	0.029	0.174	91.0	0.0019	0.614	
18/12/2001	5.94	26820	17020	12200	4556	29.2	190.7	5.1	0.99	0.027	0.153	89.3	0.0017	0.635	0.71118
16/01/2002	5.78	25860	14950	11740	4218	29.1	173.3	4.9	1.71	0.028	0.168	86.3	0.0019	0.578	
14/02/2002	5.63	26660	16320	11580	4212	28.7	172.7	4.8	1.62	0.028	0.166	94.5	0.0018	0.612	
13/03/2002	5.89	23270	7018	7180	1690	12.5	80.2	1.6	0.76	0.020	0.156	87.5	0.0018	0.302	
17/04/2002		27510	15080	11680	4685	28.8	164.3	4.8	1.40	0.029	0.175	91.8	0.0019	0.548	
12/06/2002	6.06	25220	15930	11260	6284	27.1	171.8	5.9	3.32	0.034	0.158	92.7	0.0017	0.632	
11/09/2002	6.37	25150	14670	11070	4779	30.9	175.3	5.2		0.030	0.176	83.7	0.0021	0.583	0.71115
20/11/2002	5.99	27656	15981	11432	4967	27.4	164.8	5.1		0.031	0.166	97.0	0.0017	0.578	
18/03/2003	5.73	24225	13641	10145	4129	25.4	149.3	4.3		0.029	0.170	91.4	0.0019	0.563	
09/07/2003	5.99	24293	15361	11064	6854	28.4	160.2	5.1		0.032	0.177	95.9	0.0019	0.632	
15/10/2003	6.2	25676	14935	11801	5119	29.4	162.0	5.4		0.033	0.182	92.2	0.0020	0.582	
03/03/2004	5.99	23004	12390	9847	3884	26.7	144.5	4.4		0.030	0.184	85.7	0.0022	0.539	
03/06/2004	5.83	20957	11723	8716	3313	30.0	159.1	4.3		0.027	0.188	73.7	0.0026	0.559	
07/09/2004	6	23628	12736	9603	4616	28.0	156.4	5.3		0.034	0.179	81.4	0.0022	0.539	
14/12/2004	6.02	22653	13117	9401	4373	27.3	155.2	5.0		0.032	0.176	84.5	0.0021	0.579	

(between 20 and 60 cm depth), the $^{87}Sr/^{86}Sr$ ratios are much less radiogenic (0.70963–0.71391) than in deeper horizons (0.71160–0.72981). The dramatic increase in $^{87}Sr/^{86}Sr$ ratios and mineralogical composition of the soil horizon indicate that location of the weathering front is about cm-depth. This implies that in the upper horizons the leached and altered minerals remain relatively non-radiogenic compared to the bulk digest samples. However, the A-horizon of soil #8 samples in the hydromorphic zone reveals a pretty high $^{87}Sr/^{86}Sr$, close to that of bulk digest samples, suggesting a more intense alteration releasing radiogenic strontium.

In order to define the respective sources implied in the H_2O-leaching, potential mixing lines have been defined between the rain water and radiogenic sources (biotite, bulk digest soil) or unradiogenic sources (manure, plagioclase) (Fig. 4). Table 6a summarizes the minimum and maximum percentages of each end-member allowing to explain the $^{87}Sr/^{86}Sr$ ratios of soil leachates. In Fig. 4a, the mixing curves represent the potential evolution during the H_2O-leaching experiments. None of these mixing curves explains alone the soil H_2O-leaching compositions, except the leaching of the deepest horizons which are in good agreement with biotite dissolution and do not seem to require any other contribution (curve 1). For the other shallower soil leachates, biotite and bulk digest soil (curve 5) produce too high isotopic ratios, while plagioclase and manure produce slightly too low isotopic ratios (curve 2). The $^{87}Sr/^{86}Sr$ ratio of upper H_2O-leaching reflects the contribution of Sr^{2+} from two opposite sources: relatively low $^{87}Sr/^{86}Sr$ from plagioclase and/or hog manures and higher $^{87}Sr/^{86}Sr$ from biotite and/or bulk digest soils. Neither the Sr isotopic ratios, nor the element ratios indicate a K-Feldspar contribution, which is confirmed through the bulk digest analyses (see next section). Four mixing lines (curves 6, 7, 8, 9) between the two radiogenic (biotite and bulk digest soil) and the two less-radiogenic end-members (manure and plagioclase) are also drawn. The evolution during H_2O-leaching experiments can be modelled as a curve (curves 3 and 4, Fig. 4a) which originates from the rain water end-member and is mixed with these four mixing curves (6–9). Curve 3 presents a $^{87}Sr/^{86}Sr$ ratio similar to the streams, by contrast curve 4 presents a higher $^{87}Sr/^{86}Sr$ ratio than streams. However, both curves represent a large part of the H_2O-leaching experiments. Higher $^{87}Sr/^{86}Sr$ indicate a predominant biotite contribution (deepest soils), whilst lower $^{87}Sr/^{86}Sr$ indicate a predominant plagioclase and/or hog manure contribution (top soils). The connection between rain water and mixing curves 6–9, including the H_2O-leaching and stream compositions, define four potential mixing values (A, B, C and D in Fig. 3a) of the low- and high-radiogenic end-members on curves 6–9.

Using plagioclase as the non-radiogenic end-member implies a higher biotite or bulk digest soil contribution up to a factor 10 as compared to a mixing with hog manure. This is explained by a relatively high major cation concentration in hog manure as compared to plagioclase. Whatever the low end-member, the biotite contribution seems significant as regards the quantities of manures and slurries

Table 5
Major and trace element concentrations (μg/L), Sr isotopic composition, and element ratios of stream waters at the Kerrien catchment outlet.

Date	pH	Na	Ca	Mg	K	Ba	Sr	Rb	DOC (mg/L)	Rb/Sr	Ba/Sr	Ca/Sr	Ba/Ca	Ca/Na	$^{87}Sr/^{86}Sr$
17/01/2001	6.7	20140	11520	7617	6533	26.4	101.3	6.0	2.89	0.059	0.261	113.7	0.0023	0.572	
14/02/2001	6.02	19850	11840	7500	5815	25.8	99.9	5.5	2.88	0.055	0.258	118.5	0.0022	0.596	
14/03/2001	6.16	20110	11027	7996	4433	27.3	103.8	4.4	3.12	0.043	0.263	106.2	0.0025	0.548	
11/04/2001	5.9	18880	11380	7582	4705	27.3	104.5	4.8	2.30	0.046	0.261	108.9	0.0024	0.603	0.71123
09/05/2001	6.04	19250	11330	7976	4407	30.2	113.4	4.9	1.99	0.043	0.266	99.9	0.0027	0.589	
06/06/2001	6.23	21010	10940	8336	5535	31.0	113.2	5.8	2.53	0.052	0.274	96.6	0.0028	0.521	0.71139
04/07/2001	6.45	21480	13270	9948	4338	27.2	112.2	5.1	2.49	0.045	0.242	118.3	0.0020	0.618	
01/08/2001	6.33	19710	9184	7842	2684	23.0	98.4	3.7		0.037	0.234	93.3	0.0025	0.466	
29/08/2001	8.11	20430	10110	8668	4973	26.1	109.6	5.8	3.99	0.053	0.239	92.2	0.0026	0.495	
26/09/2001	6.96	21750	10990	9226	6690	22.2	111.5	8.6	9.08	0.077	0.199	98.6	0.0020	0.505	
16/10/2001	7.23	22570	11070	9429	4100	22.0	115.4	5.4	4.32	0.047	0.191	95.9	0.0020	0.490	
14/11/2001	5.99	23870	11960	9875	4526	19.6	113.3	4.9	2.42	0.043	0.173	105.6	0.0016	0.501	
18/12/2001	6.15	24260	13410	10990	4904	21.8	121.4	4.8	2.04	0.040	0.179	110.5	0.0016	0.553	0.71141
16/01/2002	6.01	23940	11620	10280	4191	25.5	119.1	4.4	3.06	0.037	0.214	97.6	0.0022	0.485	
14/02/2002	5.94	23220	12160	9368	4389	30.3	118.5	4.6	3.01	0.039	0.256	102.6	0.0025	0.524	
13/03/2002	6.3	23810	20600	8216	4104	30.5	103.1	5.7	1.56	0.056	0.296	199.8	0.0015	0.865	0.71133
17/04/2002		25610	13170	9757	5759	35.2	128.1	5.5	1.63	0.043	0.275	102.8	0.0027	0.514	
12/06/2002	6.47	21660	12540	8333	6660	28.7	119.7	6.0	12.84	0.050	0.240	104.8	0.0023	0.579	
11/09/2002	6.51	*nd*	9855	8585	2504	23.7	103.5	3.1		0.030	0.229	95.2	0.0024	–	0.71146
20/11/2002	6.22	18994	10186	6750	5132	24.5	88.8	4.6		0.051	0.276	114.7	0.0024	0.536	
18/03/2003	5.88	19954	10240	7258	5302	26.3	93.0	4.4		0.048	0.283	110.1	0.0026	0.513	
09/07/2003	6.71	19798	7882	7477	2570	17.0	81.4	3.7		0.045	0.209	96.9	0.0022	0.398	
03/03/2004	5.93	19774	9861	7501	4858	26.6	97.9	4.6		0.047	0.271	100.7	0.0027	0.499	
03/06/2004	6.04	17527	7852	6175	3163	24.3	95.3	4.2		0.044	0.255	82.4	0.0031	0.448	
07/09/2004	6.51	20393	7301	6374	3583	14.8	76.7	4.2		0.055	0.192	95.2	0.0020	0.358	
14/12/2004	6.25	20015	9848	7751	4495	18.1	100.1	4.3		0.043	0.181	98.3	0.0018	0.492	

applied on the field (Appendix A). Since the end-member Sr concentrations and isotopic ratios are known, the source contributions can be converted into mass of material needed to be weathered or leached in order to explain a mean Sr^{2+} concentration of 20 μg/L in soil leaching solution (Table 6b). The biotite pool needed to explain soil leaching chemistry is far too large, from 179 to 2146 mg for 1 L of solution. This would be even worse to explain stream water chemistry which presents much higher Sr^{2+} concentrations. Even if the mass of manure implicated in the computation is high, it is in good agreement with the annual loads on the field (Appendix A) and seems the most reliable explanation, especially for the leachates displaying low Sr isotopic ratios.

By plotting the $^{87}Sr/^{86}Sr$ ratios versus Ca/Sr ratios, the soil leaching solutions present clearly a higher Ca/Sr ratio than that of separated minerals, except biotite (Fig. 4b), indicating a high manure contribution with a high Ca/Sr ratio, relative to granite minerals. The element ratios (Rb/Sr, Ba/Sr and Ca/Sr) are in good agreement with these observations (Fig. 5). The top soil H_2O-leachings present the larger range of Ba/Sr and Rb/Sr values, remaining below those of muscovite. Moreover, the soil H_2O-leachings are also enriched in Rb, compared to soil NH_4Ac-leaching. The deepest soil leachings present relatively high Ba/Sr, and Rb/Sr ratios which confirm the weathering of biotite and/or muscovite.

4.1.2.3. NH_4Ac exchangeable cations. Soils are leached using an NH_4Ac solution to investigate the soil ion-exchange pool (Table 3). The concentrations of leached cations are higher in the top soils than in the deeper soils by a factor of about 3 for Sr, 1.5 for Rb and K, 2–3 for Ca, Mg and Ba. The soils from Kerrien release more cations than those from Kerbernez, by a factor 2 in average.

The cation exchangeable pool has low and extremely homogeneous $^{87}Sr/^{86}Sr$ ratios, ranging from 0.70916 to 0.70952. This signature remains lower than those of river waters (~0.711), bulk digest soils and minerals, except plagioclase (0.70845). It is comparable to that of manure (~0.70950). This monotonous $^{87}Sr/^{86}Sr$ ratio in NH_4Ac-leachates strongly suggest that the topsoil, which is enriched in clay minerals, is more influenced by a non-radiogenic source, such as manures. Indeed, since manure is about 10-fold less concentrated in Sr than plagioclase, a Sr isotopic ratio close to that of manure implies that Sr in the exchangeable pool results from manure for at least 90%, considering a simple and pure mixing between the two end-members manure and plagioclase. These results suggest that the water moving through the soil, and then reaching the stream waters is not strongly influenced by manure, as proposed by several authors (Åberg et al., 1989; Bullen et al., 1996; Katz and Bullen, 1996). On the contrary, in deeper soils the low $^{87}Sr/^{86}Sr$ ratios in the NH_4Ac-leachates, different from those of stream waters and some soil H_2O-leachates suggests that the cation exchangeable component does not influence directly the surface soil solution. The cations ratios indicate a higher influence of mineral weathering, including biotite, muscovite or K-feldspar (Fig. 5), explained by the saturation of the cation exchange sites on the clay minerals for example.

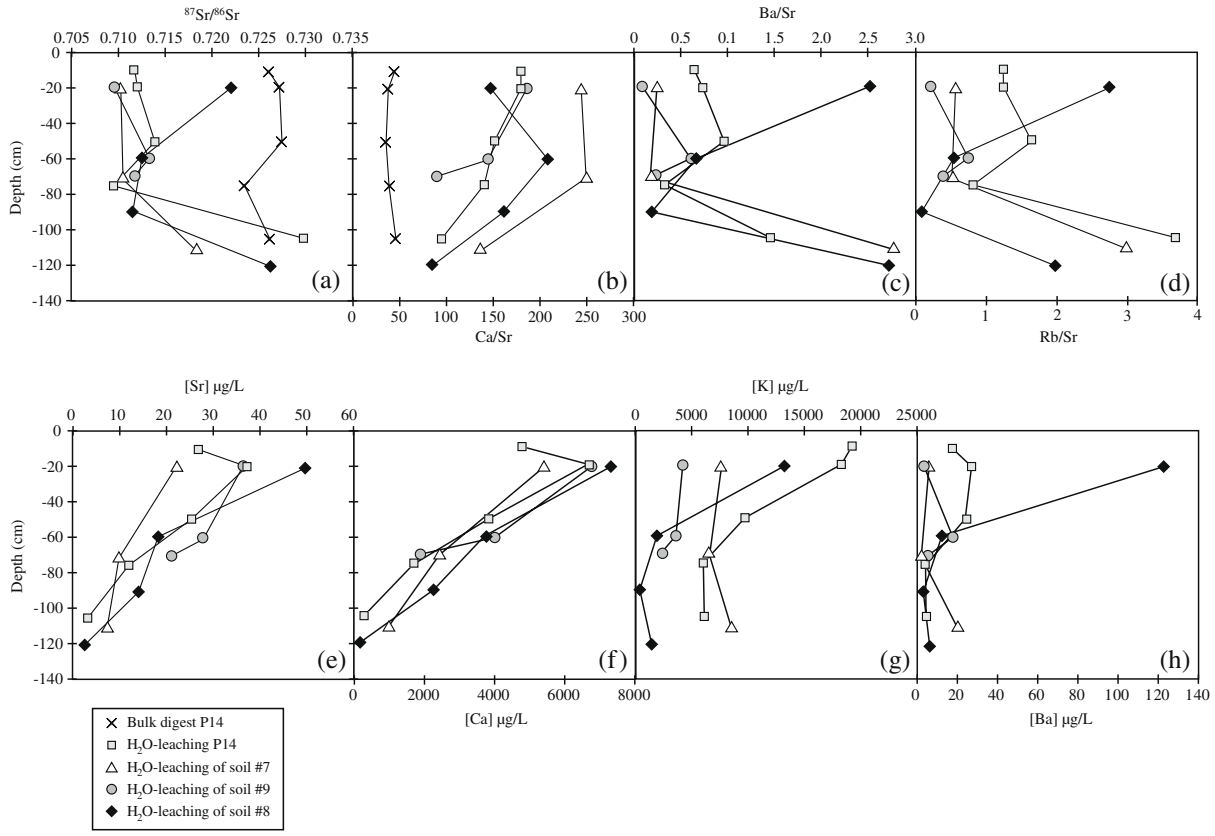

Fig. 2. Variations with soil depth of (a) $^{87}Sr/^{86}Sr$, (b) Ca/Sr ratio, (c) [Sr], (d) [K], (e) [Na], (f) [Ca] and (g) [Mg] for soils #7, #8 and #9 from Kerbernez and Kerrien.

4.1.3. Organic, mineral and chemical fertilizers

In addition to soils and rocks, major cations may be also released from anthropogenic materials, such as organic and mineral fertilizers, especially in Brittany. The main applied fertilizers are animal manures, NPK fertilizers and NH_4NO_3. Only hog manures have been analyzed for Sr isotopic composition for this study, because of the low Sr concentration of the other materials. An average $^{87}Sr/^{86}Sr$ ratio of 0.7079 for NH_4NO_3 applied in Brittany is given in the literature (Widory et al., 2004). NPK(S) fertilizers have about the same range of $^{87}Sr/^{86}Sr$ ratio (0.7072–0.7079) than ammonitrates (Riou, 1995). Hog manures (data from Widory et al. (2004), and this study, Table 1) present high Ca, Mg and K concentrations. The Sr concentration of bulk digest manure is about 63–73 ppm. Hog manures sampled in Brittany show quite homogenous $^{87}Sr/^{86}Sr$ ratios of 0.7094–0.7096. In the following discussion, the range of $^{87}Sr/^{86}Sr$ ratios includes data from this study and from Widory et al. (2004). Moreover, the hog manures are characterized and discriminated by much higher Ca/Sr than any other minerals or bulk digest soil.

4.2. Stream waters

The chemical and Sr isotopic composition of stream waters from both Kerrien and Kerbernez catchments are presented in Tables 4 and 5.

4.2.1. Major element chemistry

Stream waters from Kerrien and Kerbernez catchments display about the same major cation distribution (Tables 4 and 5). Sodium is the dominant major cation in both Kerrien and Kerbernez stream waters. Ranging from 17 to 27 mg/L, Na represents about from 42 to 54% of the total major cation content. Calcium is the second in importance (19–30%), and is about twice less concentrated than Na. However, Kerrien stream waters display a deficit of major cation relative to Kerbernez stream waters, over the same time period, of 10–50%, depending on the sampling date.

4.2.2. Strontium concentrations and $^{87}Sr/^{86}Sr$ ratios

Between 01/2001 and 12/2004, Kerbernez stream waters show a Sr concentration ranging from 145 to 190 µg/L (excepting one value at 80 µg/L), whereas the range of Sr concentration for Kerrien stream waters is 77–128 µg/L. Moreover, the Sr concentration in Kerrien streams shows the lowest value during the year 2003–2004. The $^{87}Sr/^{86}Sr$ ratios of stream waters present an extremely narrow range of variation, whatever the hydrological conditions (Fig. 3a), with a value of 0.71113 ± 0.00006 ($n = 4$) for Kerbernez and 0.71136 ± 0.00009 for Kerrien ($n = 5$). In spite of the low number of $^{87}Sr/^{86}Sr$ ratios, their variation does not reflect any range of hydrological conditions, or seasonal variations. The Sr content of open field bulk precipitation is rather low, 2–20 µg/L, with a $^{87}Sr/^{86}Sr$ ratio of 0.70892 ± 0.00001

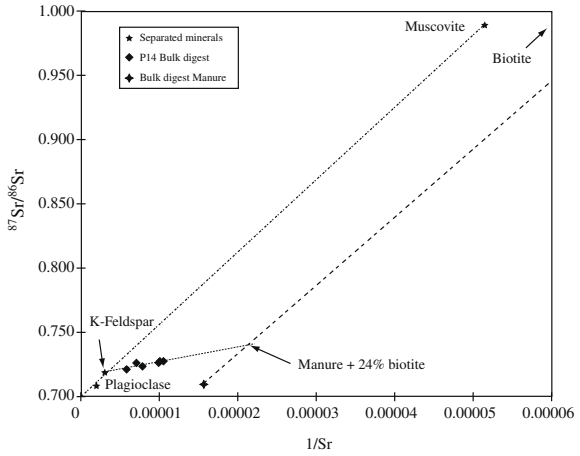

Fig. 3. Variations of $^{87}Sr/^{86}Sr$ ratio with (a) Sr concentration and (b) Ca/Sr ratio in stream waters of Kerrien and Kerbernez. Hog manures include data from this study and from Widory et al. (2004). Mixing curves represent a mixture (Table 6) between (1) biotite and rain water, (2) plagioclase and rain water. Curves (3 and 4) represent a mixing between rain water on one hand and a second mixing between manure or plagioclase and biotite. (3 and 4) represent two different contributions of biotite. Other mixing curves represent a mixture between (5) bulk digest soil and rain water, (6) manure and biotite, (7) plagioclase and biotite, (8) manure and bulk digest soil, (9) plagioclase and bulk digest soil. Here are the proportion of biotite or bulk digest soil for mixing with plagioclase or manure: (A) 24% biotite or 17% bulk digest soil, (B) 32% biotite or 65% bulk digest soil, (C) 2% biotite or 7% bulk digest soil, (D) 21% biotite or 55% bulk digest soil. Chemical composition of rain waters is available in Appendix B.

(Appendix A). This ratio is close to that of seawater, which is supported by the vicinity of the Atlantic Ocean.

4.2.3. Cation budgets

The various human-made inputs, such as fertilizers, have a range of Sr contents (3–1500 ppm) with an isotopic ratio ranging from 0.7079 to 0.7109 (Négrel, 1999; Widory et al., 2004; Table 1). An empirical estimation of cations released from the manure and slurry mineralization can be calculated through an annual mass balance. This computation is based on a hydrological water-balance. The precipitation average over a 5-year period (2000–2005) is 1235 mm, with potential evapo-transpiration of about 50% (Martin et al., 2004)). Such evapo-transpiration allows the infiltration of 500 L of rain water per m^2. The slurries and manures are applied at an average rate of 3–5 m^3/ha and 0.5–3.0 T/ha (Appendix A), respectively, on Kerrien and Kerbernez. Knowing the anthropogenic contribution, we used the cation concentrations presented in Appendix C, assuming that slurry contains between 10 and 30% of solids (Nicholson et al., 1999). Knowing the concentration of Na^+ (2.7–4.5 g/kg), Ca^{2+} (20–43 g/kg) and Sr^{2+} (0.06–0.10 g/kg) in slurries, the total mineralization of these organic matter releases between 1.2 and 14 mg/L of Ca^{2+} between 0.2 and 1.4 mg/L of Na^+ and between 4 and 30 μg/L of Sr^{2+} in streams. Considering the cation concentrations in stream waters in Kerrien and Kerbernez catchments, the organic fertilizer mineralization explains from 5 to 40% of the Sr^{2+} pool, and less than 10% of the Na^+ pool. However, the slurry mineralization releases from 20 to 100% of the Ca^{2+} encountered in stream waters.

5. DISCUSSION

5.1. Systematics in soil profiles

There are three possible sources of Sr^{2+} to soil water: (1) Sr^{2+} released from mineral weathering within the soil zone through incongruent or congruent dissolution, (2) Sr^{2+} delivered via atmospheric aerosols dissolved in rainfall and (3) Sr^{2+} delivered by additional material applied on soil, such as fertilizers. All these sources are also considered for the other major cations (Ca, Na, Mg). Furthermore, the different cations can either be released into the soil mobile water and leave the soil, or can constitute a reservoir with an intermediate mobility in the clay fraction (cation exchange pool). In order to characterize the most reliable source of Sr and other basic cations in soil water, and then in streams, element concentrations and element ratios such as Ba/Sr, Rb/Sr, Ca/Sr and Sr isotope ratios ($^{87}Sr/^{86}Sr$) have been used as tracers. Ba, Rb and Sr occur in various minerals which have a different weathering susceptibility. In this studied granitic environment, the main carrier of Ca, Sr and Na is the Na–Ca-plagioclase, while the main carrier of Rb, Mg and K is biotite, and then muscovite (Table 1). K-feldspar is an intermediate between these two end-member concentrations.

First, trace minerals enriched in Ca, such as apatite and epidote, may be considered as an important source of Ca^{2+} in stream waters (Blum et al., 2002; Oliva et al., 2004). Moreover, several authors found that disseminated calcite can have a similar effect than apatite, in controlling the chemical composition of surface and ground waters in crystalline rocks (Blum et al., 1998; Clow et al., 1997; Jacobsen and Blum, 2000; Weyer et al., 2008; White et al., 1999). The control of trace minerals may also be highlighted through Sr isotope composition (Taylor et al., 2000). Indeed, during early stages of weathering, the $^{87}Sr/^{86}Sr$ ratios of soil solutions can be controlled by the presence of reactive phases, rather than that of major minerals. However, their influence is limited once the steady-state is reached. Generally, apatite is non-radiogenic (Probst et al., 2000), and thus has a $^{87}Sr/^{86}Sr$ ratio generally lower than other silicate minerals (Aubert et al., 2001). Dissolution of apatite would be in line with the low Sr isotopic ratios of plagioclase or manure. However, several arguments allow us to rule out the accessory mineral hypothesis as a major source of Ca. (1) Neither apatite nor calcite has been observed in the granite thin sections, nor with XRD analyses, nor binocular observation. (2) Weathering is advanced and does not seem to represent an early stage. Furthermore, the Ca and Sr decrease with depth in the H_2O-leaching, and to a lesser extent in the bulk digest, does not agree with a potential source related to accessory minerals which have no reason to be located in the upper part of the soils. (3) The extremely high cation concentrations and weathering rates as compared to catchments investigated elsewhere (White

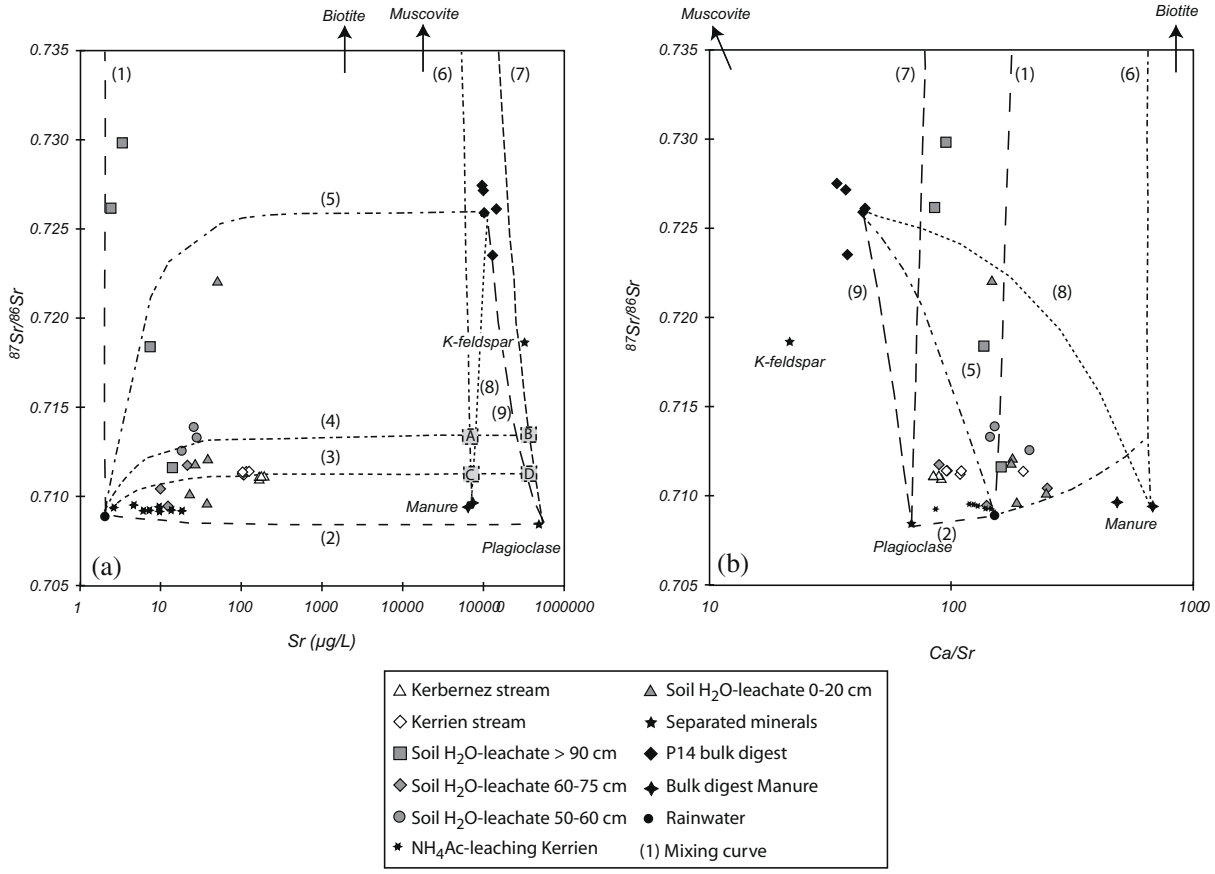

Fig. 4. Variations of $^{87}Sr/^{86}Sr$ ratio with 1/Sr for bulk digest soils, compared to separated minerals. Two correlation curves are drawn (1) between plagioclase, K-feldspar and muscovite ($R^2 = 0.9989$), and (2) between biotite and manure.

et al., 2001, 1999) imply extremely significant sources (see Section 5.3). Accessory minerals, even if they might contribute to the cation fluxes, do not play a major role in the investigated agricultural catchments.

Second, the influence of some silicate minerals, such as biotite or K-feldspar is accompanied by the contribution of manure, as suggested by bulk digest soils. This can be interpreted as the fact that manure and biotite bear a relatively similar weathering rate, which might be more important than K-feldspar. The triangular diagram plotting Rb/Sr, Ba/Sr and Ca/Sr/500 (Fig. 5) suggests that bulk digest soils are influenced by mineral sources, such as Biotite and K-Feldspar, but do agree with the potential influence of a mixture of biotite + manure. Overall, these results suggest that a large fraction of K-minerals remains to weather in soil particles. The succession of weathering reaction suggested by chemical tracers implies that K-mineral biotite is the less resistant mineral and the

Table 6
(a) Percentage of radiogenic end-members (biotite or bulk digest soil), mixed with either manure or plagioclase required to explain the Sr isotopic ratio of stream waters (from Fig. 4a). (b) Mass (in mg) of biotite, plagioclase, hog manure or bulk digest soil required to explain the concentration of 20 µg Sr/L of soil H_2O-leachates.

	Mixed with Hog manure		Mixed with plagioclase	
	Minimum	Maximum	Minimum	Maximum
(a)				
% Biotite	2	24	21	32
% Bulk digest soil	7	17	55	65
(b)				
Mass of Biotite	179	2146	1878	2861
Mass of bulk digest soil	18	28	89	105
	Mixed with biotite		Mixed with bulk digest soils	
Mass of manure	227	292	247	277
Mass of plagioclase	28	32	14	18

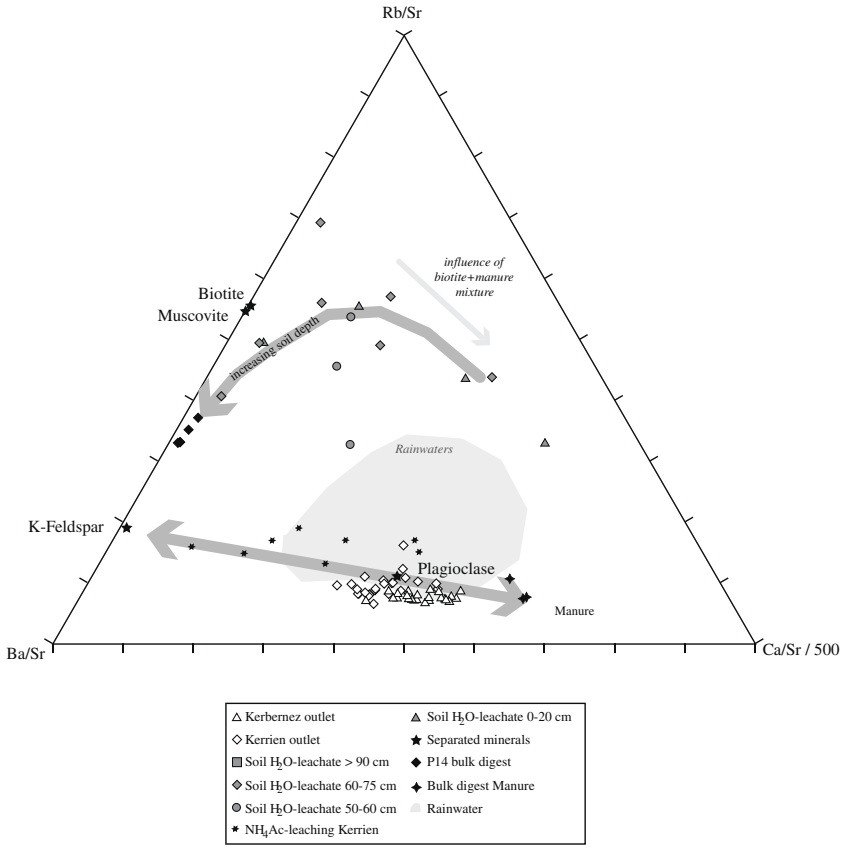

Fig. 5. Triangular diagram plotting Rb/Sr – (Ca/Sr)/500 – Ba/Sr for separated minerals, bulk digest soils, NH_4Ac- and H_2O–soil leachates, bulk digest manures and stream waters.

first to dissolve as observed in the deep soil profile, and in the saprolite (>70 cm). Biotite constitutes with manure, which is almost completely stored in the exchangeable phase, the main source of Sr^{2+} in the soil, both of them constituting a first phase of Sr^{2+} mobilization, prior to K-feldspar. A more intensive weathering, encountered in the mid-soil profile, allow the plagioclase dissolution to be a major source of elements into soil leaching solution, avoiding any major anthropogenic contribution. The plagioclase dissolution products seem to be removed from the soil itself through solution export to stream. The K-feldspar is more resistant relative to Sr isotopes, which explains that no clear contribution has been observed in soil leaching whilst it is the major source of the soil itself, as revealed by bulk digest analyses. As weathering continues, K-feldspar should become the dominant source, with muscovite which seems to be the more resistant mineral relative to Sr isotopes.

Fig. 6 summarizes all the observations and conclusions of this study. The soil leaching of different soil horizons demonstrated the influence of three different phases on the labile phase chemistry:

(1) In the top soil (0–20 cm), the manure contribution predominates and represents a high labile phase generating high major cation concentration and relatively low $^{87}Sr/^{86}Sr$ ratios in soil leaching solutions.

(2) In the mid-soils (20–70 cm), almost no influence of plagioclase is observed in the Sr isotopic composition of bulk digest soils. On the contrary, plagioclase signature is evident from H_2O-leaching. This can be interpreted as the fact that plagioclase is particularly labile and is not 'kept' in the soil neither in the solid nor in the exchangeable phase. Manure and plagioclase with a comparable low $^{87}Sr/^{86}Sr$ ratio, and a more radiogenic phase (such as bulk digest soil and/or biotite) control most of the geochemical isotopic and elemental tracers. The cations seem to be inherited from a slow weathering of the granitic rock.

(3) In the deep soil horizons and saprolite itself, a unique contribution may be revealed, with a high $^{87}Sr/^{86}Sr$ ratio, enriched in K, such as biotite or even muscovite. The weathering of such K-host mineral phases may occur below the alteration front, where the weathering processes are the most active, as suggested previously by Pavich (1986). The concomitance of high application rates of fertilizers, mineral dissolution chemical signature, and fertilizer influence on the chemistry on the surface soil, suggests that soil acidification induced by the use of fertilizers may enhance the mineral weathering in the deeper soil layers. This is contrary to some authors (Fernandez et al., 2003; Gbondo-Tugbawa and Driscoll, 2003; Sverdrup et al., 1995).

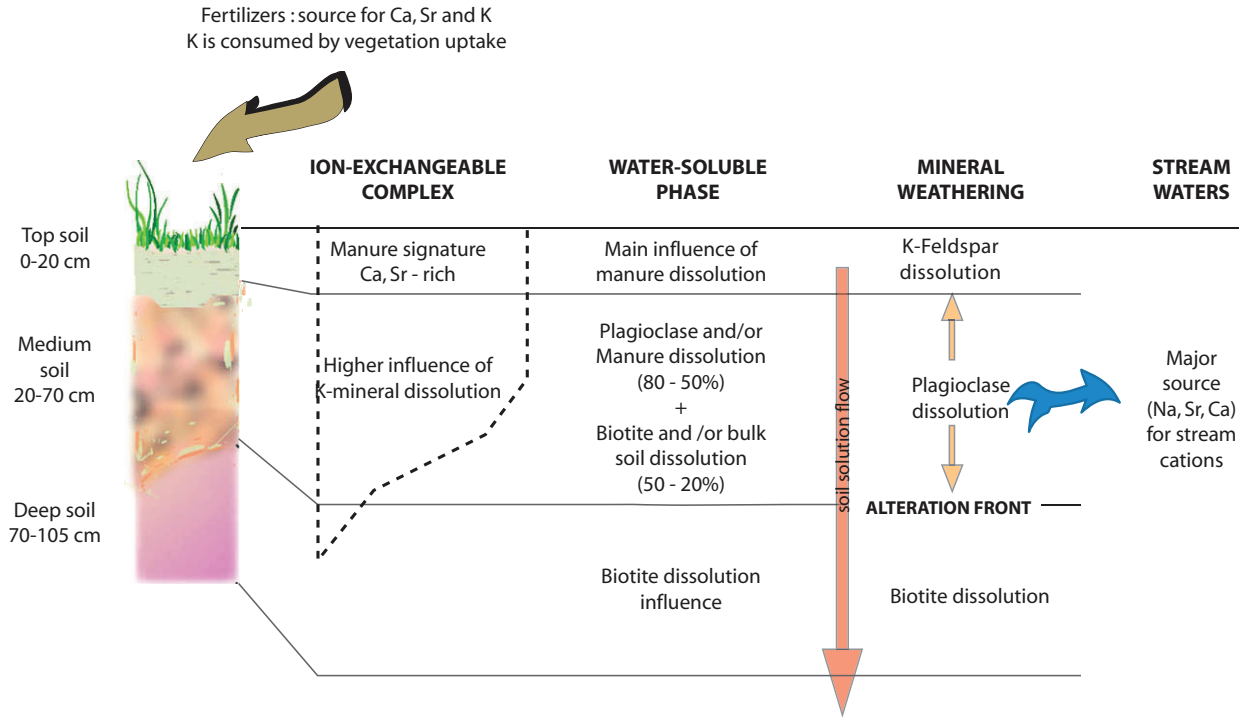

Fig. 6. Synthetic cartoon showing the evolution of cation release with depth depending on the exchangeable, labile and mineral fraction in a soil profile.

5.2. Acquisition of the chemical signature in stream waters

In anthropogenic catchments, mineral and organic fertilizers applied on soil at varying rates can alter the geochemistry of soil, ground- and stream waters. Stream chemistry is relatively sensitive to human activities, and especially agriculture, which induces rapid changes in cation release (Flintrop et al., 1996). Indeed, in the previous section we have shown that manure-derived Sr^{2+} was included in the exchangeable phase of the soil. The stream waters show definitely different geochemical characteristics from soil waters. Dissolved cation concentrations of both Kerrien and Kerbernez stream waters (Tables 4 and 5) are extremely high as compared to those found in small catchments under temperate climate conditions and on granite and granodiorite basements (Stutter et al., 2006; White and Blum, 1995). Such high cation concentrations are encountered in tropical environments where chemical weathering rates are extremely pronounced (Oliva et al., 2003; White and Blum, 1995). Stutter et al. (2002) suggested from catchment investigation in Great Britain that agricultural practices increased the Na concentrations. Na is also the dominant basic cation in both Kerbernez and Kerrien catchments. Stream waters display very high cation concentrations which are induced by (1) the KCl addition, K being largely consumed by the vegetation which requires another cation to electrically equilibrate the waters. (2) NH_4 derived from the manure addition, which acts as an acid addition since it is rapidly transformed to NO_3 in the soil (Van Miegroet and Cole, 1984). This large acidification process leads to the very high concentrations in the stream waters observed in Kerrien and Kerbernez catchments.

In the $^{87}Sr/^{86}Sr$ vs Ca/Sr diagram (Fig. 4b), the $^{87}Sr/^{86}Sr$ ratios of stream waters are specifically closer to those of soil layers dominated by mineral weathering rather than those dominated by hog manure leaching. Furthermore in the Fig. 5, there is a clear evidence that the stream waters are directly related to the plagioclase dissolution which appears as the dominant reaction. This implies that in both catchments, Na is the dominant weathering-derived cation in streams. The previous result is consistent with the low Ca/Na ratios in minerals (0.37 for Na–plagioclase) and soil (0.31). However, the Ca/Na ratios in streams are in average 0.60 for Kerbernez and 0.53 for Kerrien, respectively. Such high Ca/Na ratios, higher than that of plagioclase, have been interpreted as the result of accessory mineral dissolution (apatite or calcite) (Aubert et al., 2002; Blum et al., 2002; Clow et al., 1997; Jacobsen and Blum, 2000; Oliva et al., 2004; White et al., 1999). Here, these high Ca/Na ratios may be explained, with the lack of significant accessory minerals, either by the differential contribution of biotite (Ca/Na = 3.26), or mineralization of hog manure (Ca/Na = 10–15). The streams display Sr/Na and Ca/Na ratios ranging between those of plagioclase and biotite, whilst the manure influence is much more sensitive in the soil leaching which have much higher ratios. Although the manure influence is clear in the upper soil leaching, the high Ca/Na ratios of streams do not seem to result from agriculture product contribution. Compared to rain waters and soil leaching experiment, stream waters have relatively high Si concentration, positively correlated to Na and Mg (not shown here). This confirms that a large part of Na and Mg is directly inherited from silicate mineral weathering, respectively from Na–plagioclase and biotite, in the different soil layers, and the saprolite.

5.3. Cation solute budget

In this section, the respective role of the manure and mineral contribution to the total budget is addressed. It is important to recognize that the cation and Sr sources and contributions are estimates. Errors involved in the simple mass balance and two end-members mixtures approach include those associated with the measurements of water in a weekly scale and water chemistry on a monthly scale. However, based on a 11-year dataset, Likens et al. (1977) concluded that 1–3 years of measurements are adequate to characterize the magnitude of loss or gain of base cations, except K^+ which displays a high variability in annual inputs. However, the cation budget estimation gives a clear confirmation that (1) most of the Na and Sr budgets are not related to manure addition, and (2) the dissolved calcium in streams cannot be explained only by a water–rock interaction, but also implies the partial mineralization of manures and slurries. The fertilizer-derived Ca^{2+} pool stored in soil profile can be leached at the same time than other cations, such as Na^+ or Sr^{2+}. The main difference is that Na^+, and in a lesser extent Sr^{2+}, dissolved in streams is mostly controlled by the dissolution of Na–plagioclase (hydrolysis) in the soil, rather than any agricultural inputs.

Several environmental problems have been pointed out concerning the impact of organic and chemical fertilizers on surface and ground waters, with increasing dissolved nitrate concentrations for example. These concerns are not only confined to water quality, but also to ecology, with decreasing species diversity and increased productivity (Seitzinger and Kroeze, 1998). In Brittany, where base cations are largely exported from agricultural catchments compared to more natural catchments, the chemical weathering of silicate minerals is not the only contributor to this cation exportation. Indeed, soils may also be an important contributor, through its ion-exchange complex and its leaching by acidification process. Soil acidification, through atmospheric or agricultural deposition, can lead to irreversible decrease in clay activity with decreasing pH. Stability and cation exchange capacity of soil under temperate climate and under agricultural pressure might be a continuous and enhancing environmental concern for the next decades. Indeed, soil acidification by N-fertilizers can have significant impact on chemical aspects of soil quality, in particular on the partitioning of Al into solid phases. In addition to decreasing alkalinity, dissolved element fluxes exported by surface waters have been highlighted in a few studies devoted to agriculture impacts on chemical weathering, on a local scale (Collins and Jenkins, 1996; Pierson-Wickmann et al., in press; Semhi et al., 2000) or large scale (Perrin et al., 2008; Raymond and Cole, 2003; West and Mcbride, 2005). And in addition to cation loss by acidification, a counter effect of liming, to prevent acidification, is the loss and export of organic matter in the dissolved fraction of soil, which goes directly into streams. The increase in dissolved organic matter is also another environmental concern.

6. CONCLUSION

The chemistry of soil and stream waters was monitored in two small, adjacent, granitic catchments in Brittany, France, to evaluate the potential sources of cation solutes in the streams of both catchments. The results demonstrate that Ca^{2+} and Na^+ are the dominant weathering-derived solutes in streams. Such high concentrations mainly result from agricultural pressure. Our study investigates the origin of these solutes, analyzing Sr isotopic ratios and cation concentration ratios in the different rock minerals, soil leaching, stream water and manure chemical composition.

Soil leaching indicates a clear gradient with depth. The top soil leaching presents high cations concentrations that can mainly be related to manure addition. In the soil middle section, the cations derive from both manure addition and mineral dissolution, especially plagioclase. In the deeper part of the profile, below the soil, very low concentrations are observed with radiogenic strontium isotopic ratios which clearly indicate biotite dissolution. Finally, a mineral weathering sequence can be defined: (1) In the fresh rock, the first mineral dissolved is biotite. (2) Plagioclase dissolution is the second reaction: it appears as the dominant mechanism in the soil leaching, which in turn results from a high degree of the rock weathering. (3) K-feldspar (and probably muscovite) is the last mineral to be dissolved. In the profile investigated, the feldspar signature is dominant when the soil is entirely dissolved. It indicates that K-feldspar dissolution has not still occurred in the soil profile.

Stream waters present highly homogeneous concentrations and Sr isotopic ratios in regards to soil leaching and chemical composition or mineral composition. Several cation ratios indicate that the plagioclase hydrolysis is the dominant cation source. An influence of biotite dissolution is also observed, although less important than that of the plagioclase. It confirms that plagioclase dissolution products are not stored in the soil profile, as is the case for biotite, but are rapidly exported from the catchment. Slurries and manures remain a significant source of Ca^{2+}, and potentially Sr^{2+}, in soils. However, most of Ca^{2+} resulting from the organic fertilizer mineralization is stored in the soil ion-exchange complex.

A cation budget is computed from the chemical analysis of all the different sources. It indicates that if the Ca^{2+} originates from the manure, other cations like Mg^{2+}, Sr^{2+} and especially Si^{4+} and Na^+ which are the dominant cations in stream waters derive from mineral dissolution. The soil acidification induced by agriculture allows the mobilization of cations stored in soil layers (Ca^{2+}, Sr^{2+}). It enhances the rock weathering and accelerates plagioclase dissolution. The large cation export induced by agricultural pressure should be considered as a potential mechanism that could lead in term to soil destabilisation and agriculture productivity decrease.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.05.051.

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Appendix A: Application rates of the chemical and organic fertilizers from 1992 to 2005 on the Kerrien and Kerbernez catchments.

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Kerbernez catchment														
Ammonitrate	84.9	24.7	58.9	121.1	48.5	112.2	148.0	145.8	121.4	143.1	223.4	84.2	33.0	8.5
NPK	0	5.0	0	1.7	38.1	89.1	2.1	0	0	0	0	0	0	0
KCl	0	0	0	0	5.0	7.5	0	10.6	7.5	0	0	0	0	0
Urea	0	0	0	0	0	0	0	0	7.0	4.7	6.3	0	0	2.1
CaOMg	0	0	0	0	0	0	0	0	0	0	28.5	0	0	0
Slurry	2.5	9.9	12.0	2.9	1.2	6.1	4.0	7.5	2.9	4.9	0	6.0	6.0	6.5
Manure	0	0	0	0	0	0.5	0.4	0	1.4	0	0.9	0.5	0.7	2.3
Kerrien catchment														
Ammonitrate	183.2	283.2	206.7	128.1	167.2	114.6	172.2	137.0	127.5	142.7	122.7	194.5	37.9	222.3
NPK	0	41.1	0	61.0	92.3	13.7	10	0	0	0	0	0	92.2	102.7
KCl	0	0	0	0	0	0	0	106.6	118.4	71.0	71.0	0	0	0
Urea	0	0	0	0	0	11.8	0	0	0	0	13.7	0	0	0
CaOMg	0	0	0	0	0	0	0	0	0	0	61.6	0	0	0
Trez	0	0	0	0	0	0	0	0	0	0	0	0	0	1184.2
Slurry	0	10.9	6.6	13.1	0	0.6	3.5	3.5	5.7	1.9	6.2	4.1	1.3	1.3
Manure	0	0	0	2.2	1.1	13.4	1.9	0	0	0	7.4	4.1	7.6	4.8

The application rates are reported in kg/ha, except for slurry (m^3/ha) and manure (T/ha).

Appendix B : Major and trace element concentrations (µg/L), and Sr isotopic composition of rainwater on Kerbernez and Kerrien catchments.

Date	pH	Na	Ca	Mg	K	Ba	Sr	Rb	DOC (mg/L)	Rb/Sr	Ba/Sr	Ca/Sr	Ba/Ca	Ca/Na	Sr/Na
17/01/2001	6.59	5818	320	729	295	0.3	4.7	0.15	1.25	0.032	0.063	68.4	0.0009	0.055	0.0008
09/05/2001		2825	1263	614	180	10.5	19.7	0.24	3.02	0.012	0.533	64.3	0.0083	0.447	0.0070
06/06/2001	4.45	3997	911	670	201	1.4	13.6	0.28	-	0.021	0.101	67.0	0.0015	0.228	0.0034
04/07/2001	4.6	2298	686	415	149	0.9	10.2	0.29	5.23	0.028	0.084	67.2	0.0013	0.298	0.0044
01/08/2001	6.15	3339	703	529	624	0.9	5.1	0.71	-	0.138	0.170	136.4	0.0012	0.210	0.0015
29/08/2001	7.45	1891	1245	383	581	0.7	6.3	0.59	4.60	0.094	0.109	198.0	0.0005	0.658	0.0033
26/09/2001	6.2	1431	305	189	342	1.1	2.2	0.38	-	0.177	0.530	141.0	0.0038	0.213	0.0015
16/10/2001	5.46	8228	549	1016	448	1.2	6.1	0.36	1.93	0.059	0.198	89.5	0.0022	0.067	0.0007
14/11/2001	5.97	5562	507	646	772	1.3	4.4	0.52	3.78	0.120	0.290	116.4	0.0025	0.091	0.0008
18/12/2001	6.36	8134	563	904	804	1.6	5.5	0.67	5.04	0.122	0.282	101.7	0.0028	0.069	0.0007
16/01/2002	6.74	2021	185	234	325	1.0	1.7	0.35	2.16	0.203	0.579	107.2	0.0054	0.092	0.0009
14/02/2002	6.43	8972	559	1051	524	1.1	6.7	0.38	1.93	0.057	0.166	83.8	0.0020	0.062	0.0007
13/03/2002	6.85	11150	597	1274	844	0.7	7.3	0.59	1.85	0.080	0.098	81.7	0.0012	0.054	0.0007
17/04/2002	-	3709	517	497	441	2.3	4.5	0.41	2.54	0.091	0.511	115.6	0.0044	0.139	0.0012
12/06/2002	5.86	3304	445	425	346	0.8	3.6	0.32	2.56	0.089	0.210	122.2	0.0017	0.135	0.0011
11/09/2002	6.25	1377	260	181	401	0.3	1.8	0.45	-	0.246	0.153	141.0	0.0011	0.189	0.0013
20/11/2002	6.47	2770	361	338	327	0.6	2.4	0.36	-	0.152	0.257	150.7	0.0017	0.130	0.0009
09/07/2003	6.55	2747	1009	439	869	2.2	4.4	0.75	-	0.169	0.488	227.2	0.0021	0.367	0.0016
15/10/2003	5.07	2298	611	339	789	2.1	3.7	1.13	-	0.309	0.580	166.2	0.0035	0.266	0.0016
04/03/2004	6.47	3316	193	381	180	0.6	2.5	0.15	-	0.058	0.243	76.3	0.0032	0.058	0.0008
03/06/2004	6.24	5167	487	642	7341	1.0	5.0	1.03	-	0.204	0.189	96.5	0.0020	0.094	0.0010
07/09/2004	6.13	2325	189	289	251	0.4	2.2	0.34	-	0.153	0.158	84.5	0.0019	0.081	0.0010
14/12/2004	6.51	5296	325	613	457	0.3	3.8	0.42	-	0.110	0.091	85.5	0.0011	0.061	0.0007

Appendix C: Solute concentrations measured in mineral and organic fertilizers. Underlined data are used in the calculation.

Elements	NPK	NPK	NH_4NO_3	Urea	Pig Slurry	Pig Slurry	Pig Slurry	Pig Slurry	Pig slurry average	Dairy manure	Dairy manure
References	(1)	(2)	(1)	(1)	(2)	(3)	(4)	(5)	*	(1)	(6)
Units	$g.kg^{-1}$	$g.kg^{-1}$	$g.kg^{-1}$	$g.kg^{-1}$	$g.kg^{-1}$	$g.L^{-1}$	$g.L^{-1}$	$g.L^{-1}$	$g.L^{-1}$	$g.kg^{-1}$	$mg.L^{-1}$
Cl	*nm*	26.0	*nm*	*nm*	15.7	*nm*	*nm*	*nm*	15.7	*nm*	152.0
Na	*nm*	3.0	*nm*	*nm*	46.7	3.5	2.7	3.5	17.9	*nm*	76.1
Mg	*nm*	5.0	*nm*	*nm*	67.8	2.9	11.3	14.2	28.3	*nm*	46.7
Al	*nm*	18.8	*nm*	*nm*	4.6	*nm*	1.2	1.2	3.9	*nm*	0.03
Si	*nm*	3.5	*nm*	*nm*	15.2	*nm*	*nm*	*nm*	15.2	*nm*	6.35
K	*nm*	181.4	*nm*	*nm*	236.0	16.0	12.2	15.2	89.1	*nm*	7.7
Ca	*nm*	25.4	*nm*	*nm*	40.7	10.1	42.6	35.9	28.9	*nm*	99.1
Cr	0.03	$2.2x10^{-2}$	1.10^{-3}	$4.6x10^{-3}$	0.04	*nm*	$8.4.10^{-3}$	$1.3.10^{-2}$	$2.6x10^{-2}$	$4.6x10^{-3}$	*nm*
Mn	*nm*	0.08	*nm*	*nm*	1.4	1.2	0.6	0.5	0.6	*nm*	0.15
Fe	*nm*	1.19	*nm*	*nm*	7.0	*nm*	2.3	2.3	4.6	*nm*	0.02
Cu	2.10^{-3}	0.015	12.10^{-3}	1.10^{-3}	1.2	1.3	0.8	0.9	0.7	0.14	0.02
Zn	41.10^{-3}	0.078	5.10^{-3}	7.10^{-3}	3.0	2.5	1.4	1.0	1.8	0.19	0.07
Rb	29.10^{-3}	0.04	7.10^{-4}	4.10^{-4}	0.18	*nm*	1.10^{-2}	$1.3.10^{-2}$	1.10^{-2}	0.02	*nm*
Sr	37.10^{-3}	0.85	1.10^{-3}	1.10^{-3}	0.10	*nm*	$6.3.10^{-2}$	$7.3.10^{-2}$	0.09	0.07	*nm*
Cd	2.10^{-3}	*nm*	1.10^{-4}	1.10^{-4}	*nm*	*nm*	$5.8.10^{-4}$	$6.9.10^{-4}$	$3.4x10^{-4}$	2.10^{-4}	*nm*
Ba	2.10^{-3}	*nm*	1.10^{-3}	1.10^{-3}	*nm*	*nm*	$4.0.10^{-2}$	$3.6.10^{-2}$	$1.8x10^{-2}$	0.05	*nm*
Pb	1.10^{-3}	3.10^{-3}	3.10^{-4}	3.10^{-4}	5.10^{-4}	*nm*	$2.6.10^{-3}$	$2.1.10^{-3}$	$3.6x10^{-3}$	2.10^{-3}	2.10^{-3}
Th	*nm*	2.10^{-3}	*nm*	*nm*	2.10^{-4}	*nm*	$6.0.10^{-4}$	$1.2.10^{-3}$	1.610^{-3}	*nm*	*nm*
U	65.10^{-3}	8.10^{-3}	1.10^{-4}	3.10^{-4}	1.10^{-4}	*nm*	$5.3.10^{-3}$	$3.0.10^{-3}$	$2.2x10^{-3}$	1.10^{-3}	*nm*

(1): Mc Bride and Spiers (2001), (2): Riou (1995), (3): analyses realized on pig slurry used on Kerbernez and Kerrien catchments (data not published), (4) : Kerbernez pig slurry S4LB-161-27, (5) : Kerbernez pig slurry S1LB-161-12; (6): Widory *et al.* (2001), *nm*: not measured. Pig slurry average represents the average values of the pig slurries ((2), (3), (4), (5)) applied to Kerbernez and Kerrien catchments, used for the computation. Slurry and manure concentrations are based on dry weight.

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